IDENTIFICATION OF THERMAL PROPERTIES AND DECOMPOSITION MODELLING OF CARBON FIBERS-PPS COMPOSITES EXPOSED TO FIRE

Y. Carpier[1], F. Barbe[1], B. Vieille[1], A. Coppalle[2]

[1]Normandie Univ, INSA Rouen, UNIROUEN, CNRS, GPM, 76000 Rouen, France
Email : yann.carpier@insa-rouen.fr
[2]Normandie Univ, INSA Rouen, UNIROUEN, CNRS, CORIA, 76000 Rouen, France

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Abstract

A methodology is proposed to identify the thermal properties of a composite material and its constituants exposed to radiant heat flux with a cone calorimeter. In order to avoid compensation effects between the parameters, they are identified in several steps with genetic algorithms at different scales (macrospic model representing the whole specimen or elementary volume).

Nomenclature

	Properties		**Superscript**		**Subscrit**
ε	Emissivity	ax	Axial	m	Matrix
λ	Thermal conductivity	r	Radial	y	Yarn
$C_{p_{app}}$	Apparent heat capacity	z	Through-the-thickness	c	Composite
h	Convective heat transfer coefficient		**Others**	d	Decomposition
		T_0	Room temperature		

1. Introduction

Composite materials used for aeronautics applications can be exposed to extreme conditions such as fire exposure. The comprehension and the prediction of their thermo-mechanical behavior therefore have become of utmost important. The present work is the sequel of an experimental study dealing with the compressive behavior of C/PPS plates placed in an anti-buckling fixture (Fig. 1a) and exposed to medium radiant heat fluxes (30-50 kW/m²) with a cone calorimeter [1]. The failure of the specimens (Fig. 1b) has been linked to the decrease of the load bearing capacity of the laminates due to thermal decomposition and the formation of kink bands.

The ultimate goal of the present work is to develop a numerical model able to simulate the thermo-mechanical behavior under such testing conditions. It requires to take into account different mechanisms such as thermal degradation, thermal decomposition as well as complex boundary conditions (heterogeneous distribution of heat flux, thermal transfers with the anti-buckling fixture, convection, radiation) and the overall methodology can be divided into several points:

- Simulation of the thermal behavior before thermal decomposition;
- Development of a pyrolysis model;
- Simulation of the thermal behavior after thermal decomposition;
- Simulation of the mechanical behavior before and after thermal decomposition.

The present work is focused on the first two points. For the first one, many material properties or parameters has to be identified for each constituent i (matrix and yarns). Some of them can be easily determined from experimenl analyses (Cp_i) whereas others (h, λ_i, ε_i), or their temperature dependence might be more difficult to identify. During the past 15 years, several methodologies have been proposed to identify the materials' properties from data of bench-scale fire tests. They usually combine a 1D thermal model (often based on Henderson [2] or Gibson [3] model) and a decomposition model (mostly based on an Arrhenius equation). In their fundamental work, Lautenberger *et al.* have proposed to use genetic algorithms to estimate thermal and decomposition properties of polymers and woods [4]. Such a method leads to one value for each parameter which can be seen as a mean value over the considered temperature range. By analyzing the influence of the different parameters on the prediction of the thermal response (surface temperature or through-the-thickness temperature gradient, etc.) of glass vinylester composites exposed to fire conditions, Lattimer *et al.* have determined the material properties and the convection coefficient by means of a least square differences method [5]. More recently, Biasi *et al.* have proposed a multi-step approach on a 2D model to evaluate the thermal properties of each constituent of an UD composite and their linear temperature dependence [6]. The overral properties are first determined from simulations on a homogeneous equivalent material by using a Levenberg-Marquardt algorithm. The properties of each constituent are then calculated with an inverse homogenization technique based on Mori-Tanaka's theory.

The present work presents a multi-scale methodology based on inverse methods to identify thermal parameters from the bench-scale tests previously described. This methodology can be applied to any type of stratifications. The heat capacity and the thermal conductivity at room temperature are determined experimentally, whereas the others properties are identified from genetic algorithms by comparing experimental temperatures measured with an IR camera and simulated temperatures. To this aim, 3D simulations are first run on the *macroscopic* scale of a homogenous orthotropic plate, representing the whole specimen. By considering the heterogeneous distribution of the heat flux and the temperature of the anti-buckling fixture, it is possible to identify the mean (macro-homogeneous) properties of the composite and the heat transfer coefficient. Simulations are then performed at the *mesoscopic* scale, where each constituent (matrix and yarns) is explicitly represented, in order to identity their properties.

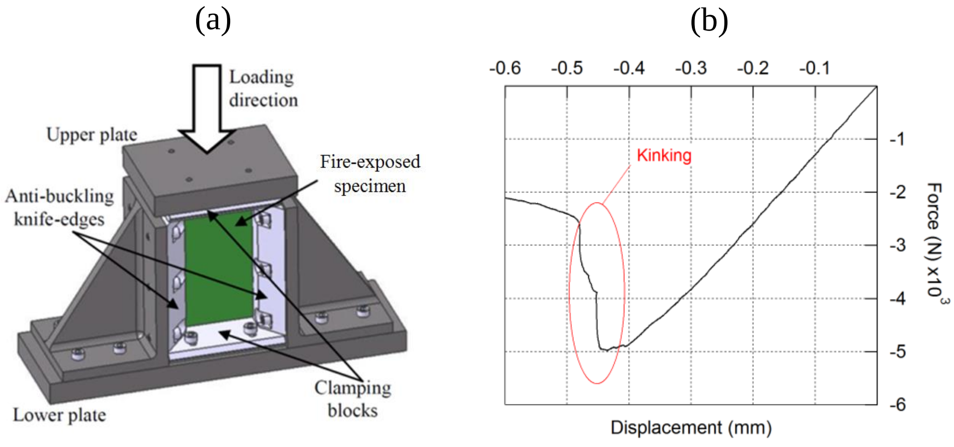


Figure 1: (a) Boeing anti-buckling fixture **(b)** Mechanical response under monotonic compression and radiant heat flux exposure

2. Materials and methods

2.1 Material and specimens

The composite material used in this study consist of 7 plies of carbon-fiber reinforced PPS prepreg laminate plates according to the following quasi isotropic lay-up: [(0/90), (±45), (0/90), (±45), (0/90), (±45), (0/90)]. The PPS resin and the PAN-based carbon fibers (T300 3K 5HS) are respectively supplied by Hexcel and Toray. The woven-ply prepregs are 5-harness satin weave fabric with a fiber volume fraction of 50%. Specimens are 150 x 100 x 2.2 mm² plates.

2.2 Materials properties characterization

The heat capacity and latent heat of melting have been measured by means of a Thermal Analysis Q2000 Differential Scanning Calorimeter. Samples were heated from 0°C to 300°C for the matrix (200°C for the composite). Three samples of resin and composite material have been tested. The thermal conductivity of the matrix λ_m and the through-the-thickness thermal conductivity of composite plates λ_c^z have been measured with a guarded hot plate system. The measurements have been conducted 4 times for each material.

2.3 Fire exposure and temperature measurements

As described in previous works [1,7], the radiant heat flux from a cone calorimeter set in the vertical configuration has been used to reproduce a fire-induced heat flux. This experimental set-up has been chosen for its compatibility with compressive testing conditions. Indeed, considering the specimen dimensions, the so-called “Boeing” anti-buckling fixture had to be used to conduct compressive tests combined with heat exposure (Fig. 1a). Though the present study does not specifically address the mechanical testing, the ultimate goal consists in simulating the thermo-mechanical behavior during compressive loading under fire. To reproduce such conditions, specimens have been placed in the Boeing fixture when exposed to heat flux. The experimental set-up is presented in Figure 2. During the exposure of the plate to the imposed heat flux, the temperature field is continuously measured on the back face of the plate by means of an IR camera (cf Fig. 5a).

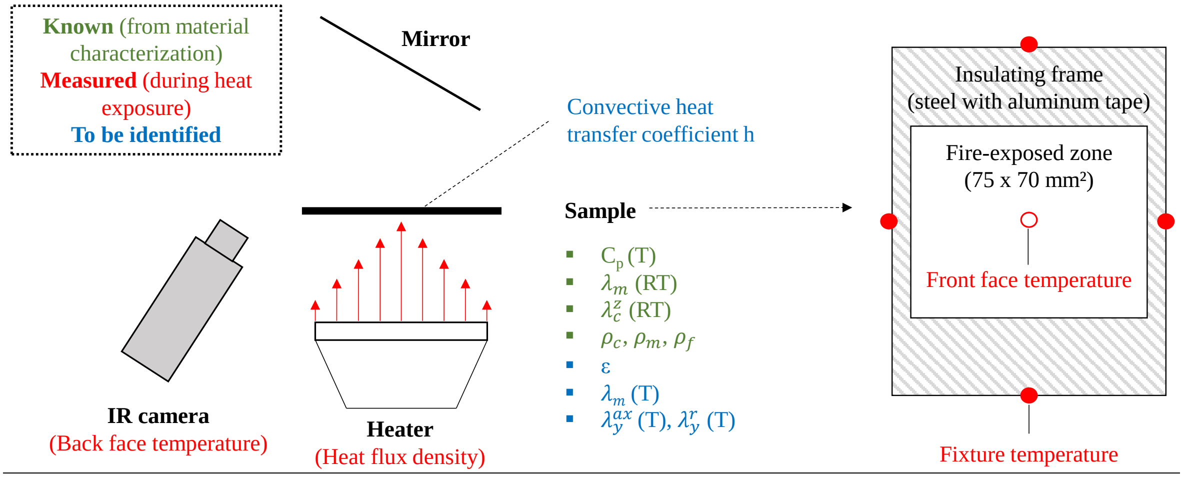


Figure 2 : Experimental set-up

2.4 Identification of properties based on temperature measurements during heat exposure

Material properties and heat transfer coefficient are identified from the optimization module of the Z-set software [8]. The basic idea is to modify a set of parameters p with an evolutionary algorithm at each thermal simulation and to compare the N_T (number of points where temperature is measured) experimental temperatures T_{exp} with the corresponding simulated temperatures T_{sim}. The objective function to be minimized is:

$$F(p) = \frac{1}{2}\sum_{i=1}^{N_T}\sum_{j=1}^{N_t} w_i\left(T_{sim}(p,t_j) - T_{exp}(t_j)\right)^2 \quad (1)$$

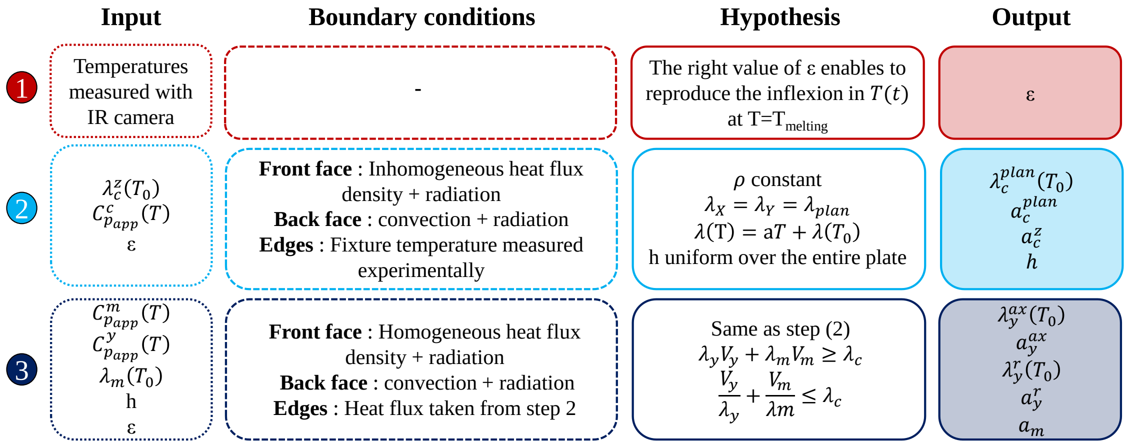
Where w_i represents the weight associated with each measurement point on the plate and N_t the number of times the temperature is experimentally acquired. A mean value of $F(p)$ is calculated every 50 runs. The algorithm is stopped when the difference between two computed mean values is lower than 1%.

The best way to identify the constituents properties would have been to perform simulations on a geometric model representing the whole specimen in which yarns and matrix are explicitely represented. However, such computations are very time-consuming and the idenfication process requires several hundreds iterations before $F(p)$ reaches its stationary value. Moreover, identifying many parameters at the same time usually leads to many valid set of parameters because of compensation effects. To avoid these drawbacks, a multi-step methodology is proposed in the present paper (Fig. 3).

The first step aims at determining the emissivity ε. The experimental values given by the IR camera depend on this value. It has been reported in the literature that an inflexion of the curve is observed on the temperature evolution during the melting of the matrix [9]. The correct value of ε is therefore the one that enables to produce an inflexion at the righ temperature (0.9 in the present case).

The second step aims at determining h. This parameter, very difficult to determine experimentally, is sometimes used as a “fitting” parameter in identification processes. Simulations are performed on a homogeneous orthotropic plate, representing the whole specimen. In this identification step $N_T = 31$ (see Eq. 1) : 1 point at the center on the exposed surface (measured with a thermocouple) and 30 points on the back face (measured with an IR camera). To ensure that the algorithm does not neglect the front face temperature (which is a critical value), the weigth associated with this point has been set to 30, and to 1 for the 30 points of the back face. The thermal conductivities are supposed to comply with a linear temperature dependence (characterized by the coefficient a_c) before thermal decomposition occurs. In addition to the identification of h, this step enables to (i) get homogenized properties to run simulations at the macroscopic scale (ii) to determine boundary conditions for the next identification step.

The remaining properties to identify are the thermal conductivities of the constituents and their temperature dependence. To this aim, an identification is carried out on a volume element (VE) of the plate in which yarns and matrix are explicitely represented. The geometric model is designed by means of Texgen software [10] and its size is 3.6 x 3.6 x 2.2 mm^3. It has the same fiber volume than the Representative Volume Element (which size is 7.2 x 7.2 x 2.2 mm^3). On the front and back faces of the VE, the same boundary conditions than on the plate are applied. On the lateral faces of the VE, heat fluxes calculated from the results of previous computations on the whole plate, are applied.



	Input	Boundary conditions	Hypothesis	Output
①	Temperatures measured with IR camera	-	The right value of ε enables to reproduce the inflexion in $T(t)$ at T=T$_{\text{melting}}$	ε
②	$\lambda_c^z(T_0)$ $C_{p_{app}}^c(T)$ ε	**Front face** : Inhomogeneous heat flux density + radiation **Back face** : convection + radiation **Edges** : Fixture temperature measured experimentally	ρ constant $\lambda_X = \lambda_Y = \lambda_{plan}$ $\lambda(\mathrm{T}) = \mathrm{a}T + \lambda(T_0)$ h uniform over the entire plate	$\lambda_c^{plan}(T_0)$ a_c^{plan} a_c^z h
③	$C_{p_{app}}^m(T)$ $C_{p_{app}}^y(T)$ $\lambda_m(T_0)$ h ε	**Front face** : Homogeneous heat flux density + radiation **Back face** : convection + radiation **Edges** : Heat flux taken from step 2	Same as step (2) $\lambda_y V_y + \lambda_m V_m \geq \lambda_c$ $\frac{V_y}{\lambda_y} + \frac{V_m}{\lambda m} \leq \lambda_c$	$\lambda_y^{ax}(T_0)$ a_y^{ax} $\lambda_y^r(T_0)$ a_y^r a_m

Figure 3: Identification methodology

2.5 Decomposition modeling: TGA

It is well established that pyrolysis kinetics highly depends on exposure conditions and that an exposure to a flame would provide more energy to specimens than samples subjected to the same temperature during TGA tests. Nonetheless, to a first approximation, it is here proposed to develop a pyrolysis model based on TGA data. To this aim, a method based on an isoconversional modelling initially proposed by Vyazovkin has been used [11]. It requires several TGA curves obtained from tests performed at different heating rates. Analyses were conducted on a TA Instruments Discovery TGA 5500 apparel under inert atmospheres at different heating rates : 5, 10, 20, 35 and 50°C.min^{-1}.

3. Results and discussion

3.1 Material characterization

The mean values measured for the thermal conductivities of the matrix and the composite are λ_m = 0.24 W.m^{-1}.K^{-1} and $\lambda_c^z(T_0)$ = 0.50 W.m^{-1}.K^{-1}. The heat capacities of both the composite and the resin have been measured from room temperature to respectively 200°C and 300°C (Fig. 3). Assuming that the linear dependence to the temperature is the same after melting (and before pyrolysis) the evolution of $C_{p_m}^{app}(T)$ is extrapolated from 300°C to 420°C. Under the same assumption, and considering a linear rule of mixture (Voigt), the evolution of $C_{p_f}^{app}(T)$ and then $C_{p_c}^{app}(T)$ can be extrapolated up to 420°C. Knowing the properties of the resin and the fibers, the evolution of the apparent heat capacities of the yarns (Vf=87%) is calculated.

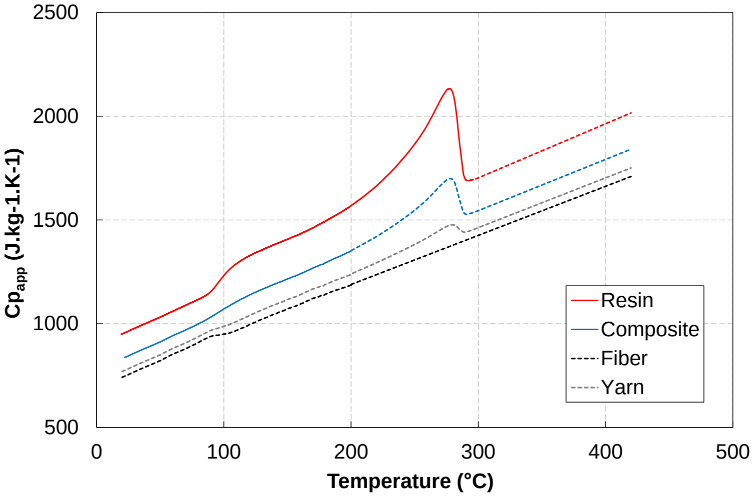


Figure 4: Evolution of $C_{p_{app}}$ for the composite and its constituents as a function of temperature (solid lines: experimental values / dashed lines: calculates values)

3.2 Thermal simulations and identification for $T_{max}<T_d$

The overall thermal conductivities and convective heat transfer coefficient identified with the macroscopic model are resumed in Table 1. The identification is based on experiments conducted with a heat flux of 30 kW/m², because the maximal temperatures induced are slightly lower than the thermal decomposition one. The value of h is close to value given by usual correlations [12]. Considering that the thermal transfert in one direction is mainly due to the fibers oriented in this direction and λ_f^{ax}=100 W.m^{-1}.K^{-1} (a value commonly used in the literature), a linear rule of mixture would provide $\lambda_c^{plan}(RT)$ =11.9 W.m^{-1}.K^{-1}. The identification also provides an increase of 2.25 10^{-2} W.m^{-1}.K^{-2} in the planar thermal conductivity, which is consistent with other values in the literature. On the contrary, the thermal through the thickness conductivity is here proved to decrease with increasing temperature. This observation contradicts the general theory that thermal conductivity increases with the temperature. As indicated by Lautenberger *et al.* [4], the parameters computed here can be seen as a mean value over the considered temperature range. Indeed, whereas λ_z is very likely to increase until T_m, its evolution after melting is not well known and very little detailed in the litterature. Thus, the model reproduces quite accurately the thermal response at 30kW/m², though it is unable to reproduce the inflexion in temperature evolution due to the matrix melting. A non linear evolution with a drop of the conductivity after the melting, could improve the model's accuracy.

Of course, the model's capability to reproduce the experimental values used for the identification does not validate the parameters. In order to validate these parameters, they were considered to simulate the thermal response under 40 kW/m² and 50 kW/m² heat fluxes (until $T = T_d$), and compared with experimental curves (Fig. 5b). The computed temperatures are below the experimental ones. This trend is more pronounced when the temperatures exceeds the range over which the thermal properites have been identified.

The identification of the parameters at the mesoscopic scale should allow the model to improve its predictive capabilities

Table 1: Identified paramaters

Macroscopic scale		Mesoscopic scale	
$\lambda_c^{plan}(T_0)$	10.7 W.m^{-1}.K^{-1}	$\lambda_y^{ax}(T_0)$	77.5 W.m^{-1}.K^{-1}
a_c^{plan}	2.25 10^{-2} W.m^{-1}.K^{-2}	a_y^{ax}	2.67 10^{-2} W.m^{-1}.K^{-2}
a_c^z	-3.5 10^{-4} W.m^{-1}.K^{-2}	$\lambda_y^r(T_0)$	6.0 W.m^{-1}.K^{-1}
h	2.5 W.m^{-2}.K^{-1}	a_y^r	-2.8 10^{-3} W.m^{-1}.K^{-}
		a_m	-3.3 10^{-4} W.m^{-1}.K^{-2}

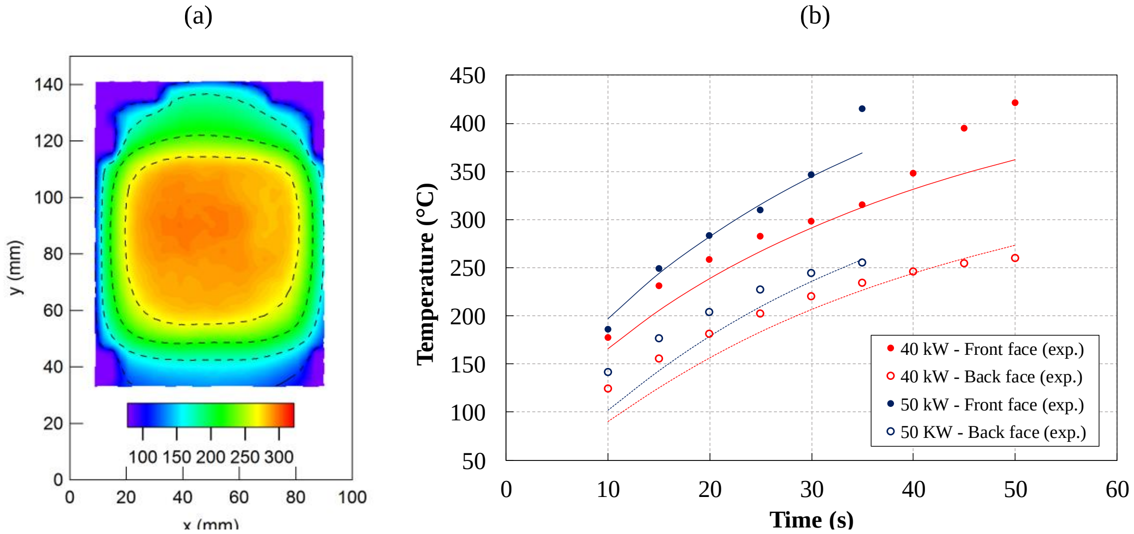


Figure 5: (a) Back face temperature field at t = 120s (30 kW/m²) (b) Comparison between experimental (points) and simulated (lines) temperatures at the center of the plate under 40 and 50 kW/m² heat fluxes

3.3 Pyrolysis model

Considering that the pyrolysis complies with an Arrhenius kinetics, the pyrolysis model consists of 3 parameters : the pre-exponential factor A, the activation energy E and a conversion function $f(\alpha)$, where α represents the pyrolys degree. These parameters satisfy Equation 2:

$$\beta \frac{d\alpha}{dT} = Af(\alpha)e^{-\frac{E}{RT}} \tag{2}$$

Where β is the heating rate. The isoconversional method assumes that E depends on the pyrolysis degree (and is consequently written E_α). For a set of n TGA conducted at several heating rates β_i, Vyazovkin showed that E_α could be calculated at any particular value of α by minimizing the function (Eq. 3) [11]:

$$\sum_{i=1}^{n} \sum_{j\neq 1}^{n} \frac{I(E_\alpha, T_\alpha^i)\beta_j}{I(E_\alpha, T_\alpha^j)\beta_i} \tag{3}$$

Where $I(E_\alpha, T_\alpha^i)$ is the so-called “temperature integral”. Once $E_\alpha = f(\alpha)$ has been determined, a conversion function has to be chosen in order to calculate A_α. It is therefore possible to establish as many pyrolysis models as there are conversion functions. A statistical analysis (F-test) carried out on 12 conversions functions showed that, with a 95% confidence level, the two best functions were the so-called “2D diffusion” and “3D diffusion” functions. These results are consistent with the study of Day on the isothermal decomposition kinetics of PPS [13].

4. Conclusions and prospects: Toward the thermal simulations for a decomposing material

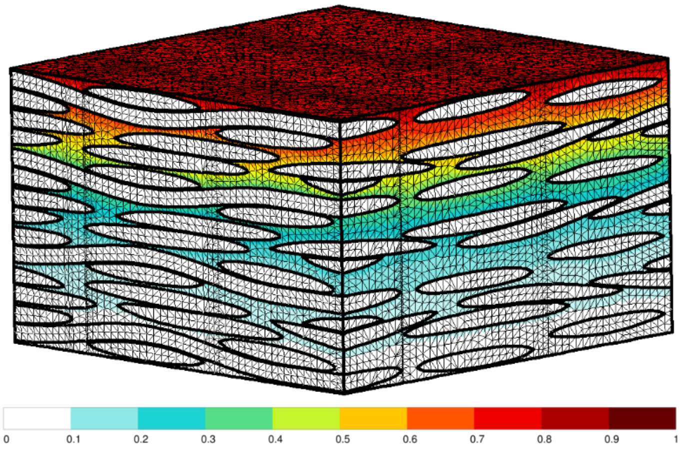


Figure 6: Repartition of the pyrolysis degree after 120 s under 50 kW/m²

The thermal properties before thermal decomposition of C/PPS laminates exposed to a radiant heat flux have been identified with a multi-step methodology based on genetic algorithms.

The ultimate goal of the present work is to simulate the thermo-mechanical behavior of a composite exposed to fire. The two first points of the overall methodology described in the introduction (simulation before thermal decomposition and development of a pyrolysis model) have been presented in this paper. The next step is to simulate the thermal behavior of a decomposed material. To do so, several authors have developed models with properties varying with the temperature and/or pyrolysis degree [14]. The model presented here is able to compute the evolution of the pyrolysis degree in the matrix based on the properties of the material just before its decomposition (Fig. 6). Of course, the thermal properties vary greatly during the thermal decomposition what must be taken into account to compute the decomposition of the material. To this aim, an identification based on the same methodology as the one described in this paper could be used, considering higher heat fluxes known to induce thermal decomposition.

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References

[1] Y. Carpier, B. Vieille, A. Coppalle, F. Barbe, M.-A. Maaroufi, Experimental study on compressive behavior under fire-exposure of carbon fibers/PPS composites, in: 20th International Conference on Composite Strucutres, Paris, 2017.
[2] J.B. Henderson, J.A. Wiebelt, M.R. Tant, A Model for the Thermal Response of Polymer Composite Materials with Experimental Verification, Journal of Composite Materials. 19 (1985) 579–595. doi:10.1177/002199838501900608.
[3] A.G. Gibson, Y.-S. Wu, H.W. Chandler, J.A.D. Wilcox, A model for the thermal performance of thick composite laminates in hydrocarbon fires, Revue de l'Institut Français Du Pétrole. 50 (1995) 69–74.
[4] C. Lautenberger, G. Rein, C. Fernandez-Pello, The application of a genetic algorithm to estimate material properties for fire modeling from bench-scale fire test data, Fire Safety Journal. 41 (2006) 204–214. doi:10.1016/j.firesaf.2005.12.004.
[5] B.Y. Lattimer, J. Ouellette, J. Trelles, Measuring properties for material decomposition modeling, Fire Mater. 35 (2011) 1–17. doi:10.1002/fam.1031.
[6] G. Leplat, V. Biasi, Méthode d'homogénéisation avancée appliquée à l'identification des propriétés thermophysiques des matériaux composites soumis au feu, in: Actes Du Congrès Français de Thermique, La Rochelle, 2015.
[7] M.A. Maaroufi, Y. Carpier, B. Vieille, L. Gilles, A. Coppalle, F. Barbe, Post-fire compressive behaviour of carbon fibers woven-ply Polyphenylene Sulfide laminates for aeronautical applications, Composites Part B: Engineering. 119 (2017) 101–113. doi:10.1016/j.compositesb.2017.03.046.
[8] Z-set | Non-linear material & structure analysis suite, (n.d.). http://zset-software.com/.
[9] A. Atreya, S. Agrawal, An experimental and theoretical investigation into burning characteristics of PPS-glass fiber composites, in: 8th AIAA/ASME Joint Thermophysics and Heat Transfer Conference, 2002: p. 2887. http://arc.aiaa.org/doi/pdf/10.2514/6.2002-2887 (accessed January 25, 2017).
[10] A.C. Long, L.P. Brown, Modelling the geometry of textile reinforcements for composites: TexGen, in: Composite Reinforcements for Optimum Performance, Elsevier, 2011: pp. 239–264. doi:10.1533/9780857093714.2.239.
[11] S. Vyazovkin, C.A. Wight, Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data, Thermochimica Acta. 340 (1999) 53–68. doi:10.1016/S0040-6031(99)00253-1.
[12] J.P. Holman, Heat Transfer 7th Edition, McGraw Hill Book Company, New York, 1990.
[13] M. Day, D.R. Budgell, Kinetics of the thermal degradation of poly(phenylene sulfide), Thermochimica Acta. 203 (1992) 465–474. doi:10.1016/0040-6031(92)85217-J.
[14] Y. Bai, T. Keller, High temperature performance of polymer composites, Wiley-VCH, Weinheim, 2014.