

Prediction of structure-properties relationships and durability of fiber-reinforced polymer composites exposed to fire

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The main objective of the present study was to develop a fire thermal model able to predict the evolution of temperature and decomposition gradient across composite structures when exposed to fire. Thermal response of composite laminates or sandwich panels, with organic polymer matrix and balsa core, was investigated under severe temperature conditions up to 750°C. In a next step, a water contribution has been included in thermal model to estimate moisture influence on the thermal response of composite materials. This enabled to propose a new approach that can be used for the prediction of hygro-thermo mechanical post-combustion properties in different fire and material scenarios.

I. Introduction

ANALYSES under extreme conditions make it possible to put a material in non-ambient conditions. The properties of that material are often drastically modified and new properties can then be studied. This occurs when a material is subjected to severe environment conditions of low or high temperature,¹ often coupled to a second stress such as an intense magnetic field, a light irradiation, a mechanical stress,² among which high pressure³ are a specific and interesting setup. Under these extreme conditions, the studied material undergoes important physical and/or chemical modifications, often leading to the appearance of metastable states or phase transitions.⁴ It is then very challenging to understand the behavior of materials under extreme conditions in order to predict and optimize their properties under normal conditions of pressure and temperature, and thus makes it possible to design new sensors having piezo- or thermo-chromic applications. Measurements in extreme conditions are both a scientific challenge, to understand the properties of materials, and a technical challenge to study the material in specific and very severe environments. The field of composite materials with organic polymer matrix and combustible cores does not escape this trend.⁵ Thus, this work is indeed focused on the analysis of the thermo-mechanical properties of both laminated and sandwich composite materials in the case of fire resistance applications, i.e. in conditions including high temperature and possibly and initial internal moisture field within the depth of the samples.

The use of composite materials has grown exceptionally in the last forty years substituting traditional engineering materials, such as steels and aluminum alloys, thanks to their higher weight-to-strength ratio, ease of manufacture and implementation, lower cost, and resistance to corrosion. This is particularly true in the marine, aircraft, aerospace and car industries. Composites materials can present some disadvantages such as a moderate heat resistance, moderate mechanical resistance or hygroscopic aging, which will be more or less important depending of choice of composite constituents. Consequently, mechanical properties of composites are susceptible to be reduced in extreme conditions. However, it is known that they present advantages compared to metallic materials, thanks to the combination of each constituent, which make it possible to take advantage of the best properties of each, to obtain a material of a performance superior to that which one would obtain by considering each material individually, combining good properties of reinforcement in the fiber direction and cohesion properties of matrix for laminate composites, or better fire and mechanical performance due to the presence of the core for sandwich composites. Nevertheless, the use of composite materials must be done with care, especially in situations that suppose risk of damage due to fire. Because of that, it is necessary to take this danger into account in the design and prevention principles, with the aim of making structures safer in terms of fire risk, understanding all the most influential phenomena regarding fire resistance of composites.

This study is focused on the description and evaluation of a hydro-thermal model capable of estimating the thermal degradation and the temperature field in the thickness of polymer composites materials. It will enable to formulate another model for the computation of mechanical properties and post-combustion for both laminated and sandwich composite structures, which will be useful to predict their durability in extreme conditions of temperature or humidity.

II. Mathematical formulation

A. Thermal model development

The thermal model proposed in this work aims to predict the mass loss due to organic polymer matrix decomposition and the temperature profiles through thickness of laminated composite materials exposed to fire, as well as other parameters such as thermal expansion, stocked gases mass and internal pressure, which are not usually modeled or evaluated in common approaches.^{6,7} The mathematical model is developed for the unidirectional heat transfer in a polymer composite laminate. It is based on the model described by Henderson, Wiecek et al.⁸ Certain assumptions must be introduced: thermal exchanges between the decomposition gases and the solid material occur until thermal equilibrium. The initiation and development of fire is decoupled and not modeled. The latter is represented as a constant heat flux which is not modified by the thermal degradation of the material. Besides, the behavior of the decomposition gases is assumed to be ideal, the gas flow will be governed by Darcy's law. Finally, the decomposition gases are supposed to be inert, i.e. they do not react. Thus, the proposed one-dimensional energy conservation equation is expressed as:

$$\begin{aligned} [m_s(x, t)c_p(x, t) + m_g(x, t)c_{pg}(x, t)] \frac{\partial T(x, t)}{\partial t} = \frac{\partial}{\partial x} \left([k_g(x, t)\phi(x, t) + k_x(x, t)(1 - \phi(x, t))] \frac{\partial T(x, t)}{\partial x} \right) \Delta x(x, t)\Delta A \\ - \dot{m}_g(x, t)c_{pg} \frac{\partial T(x, t)}{\partial x} \Delta x + m_s(x, t)A [\alpha(x, t)]^n e^{-\frac{E_a}{RT(x, t)}} [Q_p + h_c(x, t) - h_g(x, t)] \end{aligned} \quad (1)$$

$T(x, t)$ refers to instantaneous temperature at a considered point of interest, where t and x are the time and the through-thickness coordinate respectively, placed at the distance x from the front surface (i.e. the surface exposed to the heat flux), as shown in Fig. 1. Equation (1) enables to explain the thermal behavior through thickness of laminated composite materials exposed to a constant unidirectional heat flux, analyzing the three most influential energy transfer processes that manifest during thermal degradation, and susceptible to affect significantly the temperature profiles through material thickness. The first term of right member of Eq. (1) represents the induced effect on temperature $T(x, t)$ by heat conduction through the thickness. $k_x(x, t)$ and $k_g(x, t)$ are the thermal conductivity of the solid composite and gases in the thickness direction. The second term corresponds to the convection of the volatile species: the internal convection of the thermal energy due to the transport of decomposition gases $\dot{m}_g(x, t)$, which heats up by flowing towards the surface exposed to fire. The last term describes the change in temperature due to generation or heat consumption resulting from the decomposition of the matrix, considering its mass loss rate in a similar way to what Gibson et al. propose to express the material decomposition rate in his known thermal model.⁷

These terms are influenced by the increase of internal pressure of gases, as well as the thermal expansion through the variable $\Delta x(x, t)$, defined as the expansion/contraction of solid matrix $L(x, t)$, respect to the initial thickness of the sample L_0 . The parameters $m_s(x, t)$, $m_g(x, t)$, $c_p(x, t)$, $c_{pg}(x, t)$, are the solid laminate and gases mass, and specific heat of solid laminate and gases. Q_p is the endothermic decomposition energy of the polymer matrix. $\dot{m}_g(x, t)$ is the mass flow of volatile products. $h_s(x, t)$ and $h_g(x, t)$ are the enthalpies of the solid laminated composite material and volatiles.

We have modeled the resin decomposition in mass terms following a typical Arrhenius law:

$$\frac{1}{m_{m0} - m_{mf}} \frac{\partial m_m(x, t)}{\partial t} = -A [\alpha(x, t)]^n e^{-\frac{E_a}{RT(x, t)}} \quad \text{with} \quad \alpha(x, t) = \frac{m_m(x, t) - m_{mf}}{m_{m0} - m_{mf}} \quad (2)$$

A , E_a and n are the reaction rate constant, the activation energy of the decomposition reaction and the reaction order, while $m_m(x, t)$, m_{m0} and m_{mf} are the instantaneous, initial and final mass of the polymer matrix respectively, all of which can be determined in practice from thermo-gravimetric analysis (TGA) of the polymer matrix. In Eq. (1) and Eqs. (2), $\alpha(x, t)$ represent the fraction of virgin material remaining in the solid matrix, and it is used as a local variable to account for the degree of advancement of the decomposition process, allowing to distinguish between the instantaneous fraction of the virgin material and the remaining material (i.e. char material) which appears during material decomposition.

Thermal properties of partially degraded composite material are modeled using homogenization laws between virgin and char states of the composite,⁹ because information on the progress of the pyrolysis reaction is not easily available with current means. They enable modeling the local thermal properties as a function of time and through-thickness coordinate, owing to mean-field homogenization approaches, considering the progress of decomposition through $\alpha(x, t)$.

In addition, others partial differential equations must be formulated for the through-thickness thermal expansion $L(x, t)$,⁸ and material permeability $\gamma(x, t)$,⁸ depending of char and virgin material properties.

The gas storage in the solid matrix and the gas mass flow are calculated by the simplified mass conservation equation,¹⁰ which lets explain the phenomena of transport of decomposition gas through the material thickness, related

to the decomposition rate expressed by Eqs. (2). The transport rate of the mass flow of gases, $\dot{m}_g(x, t)$, can be expressed using the Darcy's equation.⁸ Besides, the internal pressure $P(x, t)$ is defined by the ideal gas state equation modified by the porosity of the material, which allows to take implicitly into account the influence of the pressure due to the gas storage in the material in Eq. (1), whose term of conductive heat transfer is modified by the porosity. Equation (1) is also coupled with the thermal expansion equation: thermal expansion being actually partly explained by pressure changes.⁹

Initial and boundary conditions (i.c. and b.c.) must involve all unknowns of the problem to close the thermal problem and become it numerically solvable. They are written as follows:

$$\begin{aligned} \{T(x, 0), m_m(x, 0), \dot{m}_g(x, 0), m_g(x, 0), P(x, 0), L(x, 0)\} &= \{T_\infty, m_{m0}, 0, m_{g0}, P_0, L_0\}, \text{ for } 0 \leq x \leq L \\ - [k_g(x, t)\phi(x, t) + k_x(x, t)(1 - \phi(x, t))] \frac{\partial T(x, t)}{\partial x} \Big|_{x=0} &= [\varepsilon_s q''_{rad} - \sigma \varepsilon_{sup} T^4(x, t)] + h_{sup} [T_\infty - T(x, t)], \text{ for } x = 0, \forall t > 0 \\ - [k_g(x, t)\phi(x, t) + k_x(x, t)(1 - \phi(x, t))] \frac{\partial T(x, t)}{\partial x} \Big|_{x=L} &= \sigma \varepsilon_{inf} [T^4(x, t) - T_\infty^4] + h_{inf} [T(x, t) - T_\infty], \text{ for } x = L, \forall t > 0 \\ \dot{m}_g(L, t) = 0, \quad P(L, t) = P_s, &\text{ for } x = L, \forall t > 0 \end{aligned} \quad (3)$$

The energy balance at the hot surface ($x = 0$) of the composite sample is described by the Stefan-Boltzmann law, considering a combination of a radiative term for the heat transfer from the heating source (q''_{rad}) to the composite during exposition to fire and also a thermal convection term of the heating source.¹⁰ By analogy, the boundary condition on the composite face not exposed to the heat source ($x = L$) is also written as the sum of radiative and convective contributions. ε_s is the emissivity of the source, ε_{sup} , ε_{inf} and h_{sup} , h_{inf} are referring to the emissivity and convection coefficients at the front or back surface of the composite. σ is Stefan-Boltzmann's constant.

The thermo-chemical degradation problem for composite materials is well defined by the set of Eqs. (1), (2), continuity, expansion, permeability, gas flow rate and pressure equations, with initial and boundary conditions described by Eqs. (3). All variables involved in their formulation, which represent the unknowns of the problem, are all coupled with each other, and express instantaneous local magnitudes. The problem is mathematically represented by a non-linear system of Partial Differential Equations (PDEs) with variable source terms and b.c. (in time and in space) that must be solved numerically for each step of t and x , and simultaneously for mass, temperature, gas transport rate, thermal expansion, gas storage, pressure and permeability, due to the complexity of the coupling of all variables involved.

A numerical method has been implemented in *Mathematica*[®], in order to solve the problem by the Method of Finite Differences. It is necessary that the PDEs problem is well posed as an initial value problem (Cauchy) in at least one dimension. The thermal problem satisfies this condition, with Dirichlet's i.c. ($t = 0$) and with Neumann b.c. ($x = 0$) and ($x = L$), expressed as a function of $T(x, t)$ and its derivative. This numerical method enables to obtain interpolation functions as the results to unknowns, in order to evaluate them as a function of time and through-thickness coordinate.

B. Hygro-thermal model development

Moisture in composite materials can considerably affect the thermal behavior and consequently the durability and global properties (physical and mechanical),^{11,12} even more for composites aged in hygroscopic environments or depending on the nature of its polymer matrix. Thus, thermal model presented in Section II.A has been improved to consider the water mass fraction that could be contained inside the material at the initial state. Due to the problem complexity, we have made some additional assumptions to model the hygro-thermal response of polymer composite materials exposed to a constant heat flux, related to moisture desorption mechanisms. The initial water content is taken into account as an additional mass contribution to the control volume of the solid material analyzed. We consider a first step of free water desorption, (which does not form bonds with the molecular network of the polymer matrix and that can be assumed from a first instance stored in material *porosities* or in the so-called *free-volume*). Then in a second step, bounded water is considered, which will be evacuated at slightly higher temperatures because of the weak bonds formed between these water molecules and the molecular network of the polymer matrix.

Water desorption has been modeled using an additional Eq. (4), which must be included in the PDEs system to solve. It is based in dehydration equation proposed by Sand et al.,¹³ but modified and expressed as a partial differential equation for the water mass loss as function of t , x , total mass of the composite and instantaneous $T(x, t)$:

$$\frac{\partial m_{H_2O}(x, t)}{\partial t} = - \frac{\partial}{\partial t} \left(\frac{m_{composite}(x, t) c_p(x, t) [T(x, t) - T_{sat}]}{\Delta h_{fg}(x, t)} \right) \quad (4)$$

In Eq. (4) mentioned above, $m_{H_2O}(x, t)$ is the instantaneous water mass contained inside the material. T_{sat} is the fibers saturation temperature, which is equal to the water evaporation temperature ($T_{sat} = 373.15 \text{ K}$) in the first step of desorption of free water (boiling water which has not formed any bonds with the polymer network). This temperature is

slightly higher in the second step of bounded water and is calculated as the temperature at which $m_{H_2O}(x, t)$ reaches the value X_{fsp} , which represents $m_{H_2O}(x, t)$ at fiber saturation point.¹³ $\Delta h_{fg}(x, t)$ is the latent heat of water, depending of $T(x, t)$ and water mass fraction $X_{H_2O}(x, t)$ for the step of desorption of bound water. It takes different expressions for free liquid and bound water as proposed in Eqs. (5):

$$\Delta h_l(x, t)[J/kg] = 1000 [3179 - 2.5T(x, t)] \text{ and } \Delta h_{desorp}(x, t)[J/kg] = 1000 \left[1176.2e^{-15X_{H_2O}(x, t)} \right]$$

$$\Delta h_{fg}(x, t) = \{ \Delta h_l(x, t), \Delta h_{fg}(x, t) = \Delta h_l(x, t) + \Delta h_{desorp}(x, t) \}, \text{ for } \{ X_{H_2O}(x, t) \geq X_{fsp}, X_{H_2O}(x, t) < X_{fsp} \} \quad (5)$$

With Eqs. (5), the processes of composite material dehydration can be explained. For the first step of free water desorption, only evaporation heat $\Delta h_l(x, t)$ of free liquid water is required up to X_{fsp} . Then, for the second step of bound water desorption, an additional heat of desorption Δh_{desorp} must be added to break the strong bonds between water molecules and the matrix network. Following this approach, it makes it possible to express the water mass loss in a similar way as resin mass loss, as shown in Fig. 1 in order to represent the hygro-thermal degradation of composites.

We note the variable control cell during the desorption process and decomposition of resin matrix, represented by the variable $\Delta x(x, t)$. First, the material is supposed to consist of different elements in the through-thickness direction x , and at each element there is a mass of fibers, a mass of water and a mass of polymer matrix. Over time, water starts to be evacuated by evaporation mechanics, following Eq. (4). Polymer matrix begins to decompose with the release of volatile substances, and matrix mass loss progressively evolves through thickness, according to Eqs. (2). At the end, the entire matrix has been degraded, leaving a char residue and fibers, which are assumed not to decompose due to considered low-medium heat flux. This modeling makes it possible to evaluate local quantities, at each through-thickness coordinate x and over time, based on certain global quantities such as the initial and final mass of the matrix and water content, and the fibers mass.

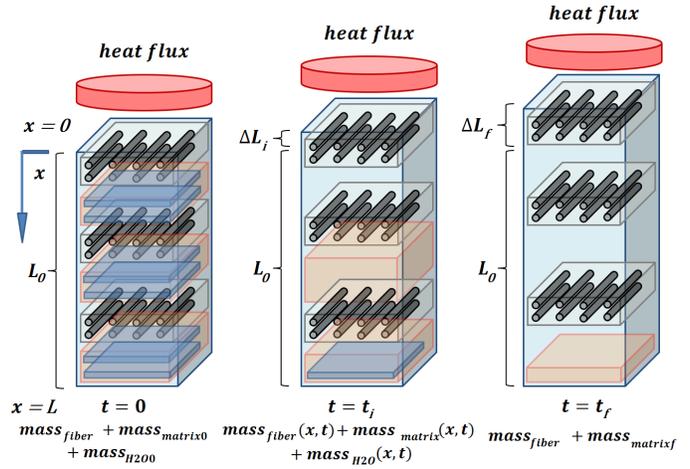


Fig. 1 Schematic of hygro-thermal expansion modeling of a laminated composite material

The heat equation Eq. (1) must be modified in order to explicitly consider the water content:

$$\left[m_{composite}(x, t) (c_p(x, t) + c_{pvH_2O}(x, t)) + m_g(x, t)c_{pg}(x, t) \right] \frac{\partial T(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ [k_g(x, t)\phi(x, t) + k_x(x, t)(1 - \phi(x, t))] \frac{\partial T(x, t)}{\partial x} \right\}$$

$$\Delta x(x, t)\Delta A - \dot{m}_{total}(x, t)c_{pg} \frac{\partial T(x, t)}{\partial x} \Delta x - \frac{\partial m_{composite}(x, t)}{\partial t} [Q_p + h_c(x, t) - h_g(x, t) - h_{vH_2O}(x, t)]$$

With $m_{composite}(x, t) = m_m(x, t) + m_{fiber} + m_{H_2O}(x, t)$ and $\dot{m}_{total}(x, t) = \dot{m}_g(x, t) + \dot{m}_{vH_2O}(x, t)$

$$\text{And } \frac{\partial m_{composite}(x, t)}{\partial t} = -m_{composite}(x, t)A \left[\frac{(m_m(x, t) - m_{mf})}{(m_{m0} - m_{mf})} \right]^n e^{-\frac{E_a}{RT(x, t)}}, \text{ for } m_{H_2O}(x, t) = 0 \quad (6)$$

The influence of water in Eqs. (6) is explicitly considered in the total mass of composite, and in the production rate of volatiles, considering water vapor because of material desorption. The specific heat of the composite material has been modified by adding an additional contribution of the water mass contained in the material, $c_{pvH_2O}(x, t)$, which lets calculate an extra contribution to enthalpy $h_{vH_2O}(x, t)$, to assure energy conservation in Eqs. (6).

The mass conservation equation must be adapted in order to consider the water mass contribution. That allows to distinguish the calculation of volatiles mass storage and pressure of evaporation and matrix decomposition processes, in order to evaluate individually the contribution of each process, as shown in Eq. (8), with the subscripts g and vH_2O referring to gases produced by matrix decomposition and water vapor, respectively:

$$-\frac{\partial m_{composite}(x, t)}{\partial t} = \frac{\partial m_g(x, t)}{\partial t} + \frac{\partial \dot{m}_g(x, t)}{\partial x} \Delta x + \frac{\partial m_{vH_2O}(x, t)}{\partial t} + \frac{\partial \dot{m}_{vH_2O}(x, t)}{\partial x} \Delta x \quad (7)$$

New initial and boundary conditions that involve the new variables related to water content must be included:

$$m_{H_2O}(x, 0) = m_{H_2O0}, m_{vH_2O}(x, 0) = m_{vH_2O0}, P_{vH_2O}(x, 0) = P_{vH_2O0}, \text{ for } 0 \leq x \leq L$$

$$\dot{m}_{vH_2O}(x, 0) = 0, P_{vH_2O}(L, t) = P_{vH_2O0s}, \text{ for } x = L, \forall t > 0 \quad (8)$$

This new formulation of hygro-thermal problem provides the temporal and through-thickness evolution of all variables involved, explicitly depending on water content, because of coupling of each other.

C. Hygro-thermal model for sandwich composites

It is known that sandwich composites present advantages compared to composite laminates,¹¹ thanks to the combination of different materials, to take advantage of best properties of each and obtain a material of a performance superior to that which one would obtain by considering each material individually. They have better fire performance due to the presence of the core, and mechanical properties significantly superior to monolithic structures. Thus, it is necessary to understand all the most influential phenomena regarding fire resistance of sandwich composites.⁹

In particular, water content can be even more influent on the thermal behavior of sandwich materials. Thus, thermal and hygro-thermal models presented in Sections II.A and II.B for composite laminates have been adapted to estimate the hygro-thermal response of sandwich composites with polymer laminated skins and combustible core exposed to a constant heat flux, considering the water mass fraction that can be contained inside the material, both in skins and in the core, especially in the case of porous core materials as balsa wood. It is necessary to added on thermal model a certain amount of resin that will be filtered inside the balsa core porosities, because of manufacturing process, so that there will be a resin diffusion in the balsa core, as represented in Fig. 2(a). We have made some additional assumptions related to desorption mechanisms. The initial water content is taken into account as an additional mass contribution to the control volume of the solid material analyzed, which is mostly stored inside porosities of skins and the core, and to a lesser extent in the molecular network and organics fiber of the polymer matrix and core respectively, as shown in Fig. 2(a). We consider a first step of free water desorption, and a second step of bounded water, for each component of the sandwich, in a similar way and it was exposed for laminates in Section II.B.

System of energy conservation equations can be expressed as Eqs. (6), using different material properties and kinetic thermal decomposition parameters depending of the constituent and its local position related to global thickness of the sandwich, because the thermal behavior of each one will be influenced by the constituent location.¹⁴ As it seems evident, mass degradation will start at front skin, and it progresses in function of time and through-thickness direction, always that heat flux be high enough to activate pertinent degradation reactions of front skin (fs), core (c) and back skin (bs), which must be also expressed individually for each constituent from Eqs. (2).

This model considers unit control volumes for each component of sandwich; upper skin, core and lower skin. This enable to calculate the instantaneous mass of each component individually. Therefore, it is necessary to weight the thickness of each part of the sandwich for the calculation of the overall instantaneous mass loss of the sandwich structure and the remaining mass during fire exposure.¹⁴ The evolution of temperature $T(x, t)$ and instantaneous mass of each component will have to be calculated separately; since they have different kinetics of decomposition. Thus, unit volumes of each constituent should be converted to real volumes, relative to the thicknesses of each material, in order to calculate the mass contribution of each component to the total mass of the sandwich, as shown in Fig. 2(b):

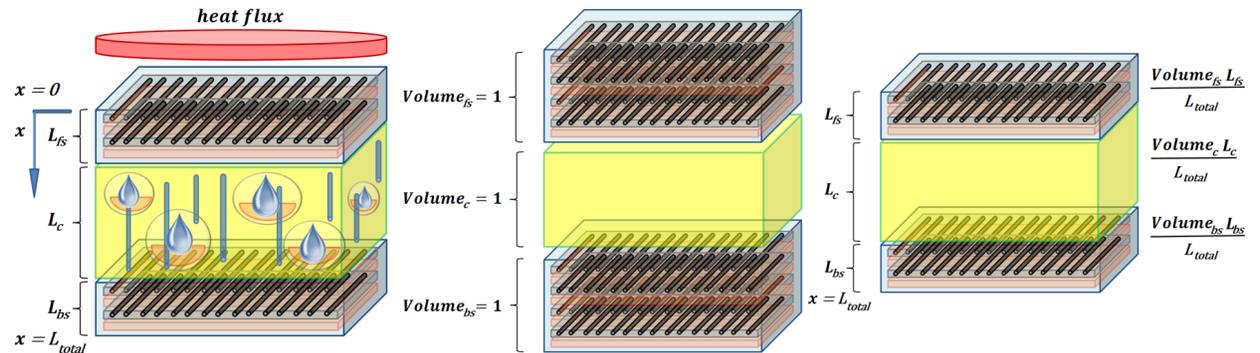


Fig. 2 (a) Scheme of hygro-thermal model for sandwich composites exposed to fire considering resin diffusion inside balsa core and moisture absorption. (b) Schema of the conversion of unit control volumes to real volumes

The instantaneous total mass of the sandwich can be normalized to its initial mass $m_{sandwich0}$ to analyze the overall weight loss of the sandwich structure. The expression of the total Remaining Mass Fraction of the sandwich material $RMF_{sandwich}(x, t)$ over time and as a function of abscissa x is given by Eq. 9:

$$RMF_{sandwich}(x, t) = \frac{m_{fs}(x, t)L_{fs} + m_c(x, t)L_c + m_{bs}(x, t)L_{bs}}{m_{sandwich0}L_{total}} \quad (9)$$

Mass conservation, expansion and pressure equations must be also formulated for each constituent of sandwich composite since they have a heterogeneous behavior. Initial conditions must be applied for all unknowns involved in the problem. However, boundary conditions must be established for the whole sandwich, that means for the upper surface of the front skin and for the lower surface of the back skin, by analogy to Eqs. (3).

D. Post-combustion mechanical response

Post-combustion (PC) properties enables to evaluate the decrease of the residual mechanical properties of the material after a certain time of exposure to fire (degradation or combustion time), once the fire has been extinguished after this time, and the material cooled down back to the ambient temperature. These properties are used to evaluate the residual mechanical integrity and safety of the structure where the material is used. It can be experimentally measured by three point bending flexural tests on thermal aged samples, in order to be able to measure the evolution of the flexural modulus as a function of degradation time.¹² Residual PC properties of composite materials are closely related to the thermal model, due to the dependence of temperature $T(x, t)$ and mass loss of the analyzed material through $\alpha(x, t)$ on mechanical properties. However, they can be calculated in a first approximation decoupled from the equations of the thermal model, through the results obtained from the evaluation of the thermal or hygro-thermal model.

For numerical computation of the normalized flexural modulus (NFM), we assume that the material thermally aged can be represented by a two-layer model as shown in Fig. 3(a) (for a laminate) and Fig. 3(b) (for each constituent of a sandwich). The first layer represents the region of the supposedly completely decomposed material (char material) after exposure to a heat flux, whose mechanical properties are weak, while the second one represents the region of the material that retains the mechanical properties of virgin material.¹⁵ The calculation takes into account the evolution of the boundary between the two regions (char and virgin materials), which is called the combustion advancing front (CAF). In the case of sandwich structures, we define three CAF: one for each constituent. Each CAF is directly related to the degree of degradation through the parameter $\alpha(x, t)$, which depends of the through-thickness coordinate x of interest. Thus, the combustion advancing fronts of each constituent are related between each other.

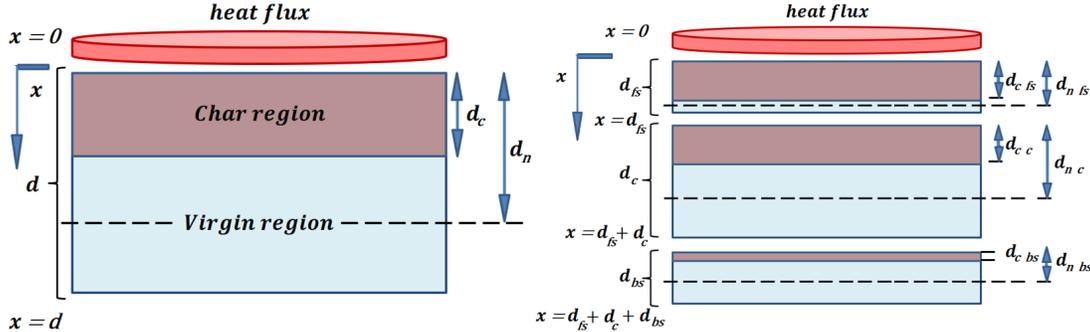


Fig. 3 Scheme of the idealized two-layer model for studying the post-combustion mechanical properties of (a) laminated composite material and (b) sandwich composite material

In Fig. 3, d represents the total thickness of the sample, d_n is the thickness from the frontal surface to the neutral axis of the material. d_c is the thickness of the carbonized layer, which is calculated from the CAF. It is the key parameter to calculate PC properties, being a function of the material degradation and evolving with exposure time to fire.

In order to evaluate the loss of stiffness, it is possible to calculate the decrease of the flexural modulus (FM) as a function of the CAF. The interface between the two regions is defined as the thickness at which the mass loss fraction reaches a certain level of degradation. Zaih et al.¹⁵ have proposed the following expressions to calculate the FM:

$$\langle EI \rangle = \left\{ \frac{4[d - d_n(x, t)]^3 + 4[d_n(x, t) - d_c(x, t)]^3}{d^3} + 4 \frac{E_c}{E_0} \frac{[d_n(x, t)]^3 - [d_n(x, t) - d_c(x, t)]^3}{d^3} \right\} \langle EI \rangle_0, \quad d_n(x, t) = \frac{d^2 E_0 - d_c^2(x, t) [E_0 - E_c]}{2dE_0 + 2d_c(x, t)E_c - 2d_c(x, t)E_0} \quad (10)$$

With E_0 and E_c the initial and final Young's modulus, related to virgin and char materials respectively. I denotes the quadratic moment of the section of the analyzed sample, and $\langle EI \rangle_0$ is the initial flexural modulus. If the properties of the carbonized material are considered negligible compared to the initial properties ($E_0 \gg E_c$), we can simplify the previous expressions assuming that $E_c = 0$, and we can calculate the NFM as $\langle EI \rangle / \langle EI \rangle_0$.

In the case of sandwich composites, Eqs. (10) enables to immediately calculate the temporal evolution of FM, for each constituent; front skin, core and back skin; through the CAF of each one. Calculus of FM of the whole sandwich must be done related to neutral section of the global sample. Theulen and Peijis proposed an expression of equivalent flexural modulus (EFM) of symmetric sandwich composites at ambient temperature. That formulation can be expanded in order to take into account the contribution of inertial terms of skins applying the Steiner's theorem respect to the neutral axis of sandwich, considering d_m as the thickness between the middle of a skin and the middle of the core:

$$\langle EI \rangle_{eq} = E_{core} I_{core} + 2E_{skin} \left(I_{skin} + S_{skin} d_m^2 \right) \quad (11)$$

For sandwich exposed to fire, thermal degradation of each of its constituents is established independently, and can

be successive or simultaneous, depending on coupling between each other. That induces a different value of E_{skin} for the upper and lower skins (index fs and bs respectively). Thus, EFM can be expressed as follows:¹²

$$\langle EI \rangle_{eq} = E_{core} I_{core} + \left[E_{skin}(x, t) \left(I_{skin} + S_{skin} d_m^2 \right) \right]_{fs} + \left[E_{skin}(x, t) \left(I_{skin} + S_{skin} d_m^2 \right) \right]_{bs} \quad (12)$$

III. Results and discussion

A. Hygro-thermal degradation estimation

Numerical results have been obtained to simulate the hygro-thermal degradation of different composite materials (laminates and sandwiches). Temperature profiles and mass loss evolution can be calculated using the thermal and hygro-thermal model exposed in the previous Sections II.A and II.A respectively. Results of thermal model are confronted with experimental data from others authors to probe and check its validation in a first part,^{11,16} and be willing to compare them with results of hygro-thermal model in a second part.

In this paper, we present the simulated hygro-thermal behavior of a laminate of E-glass fiber mat (800 g/m^2) and an unsaturated polyester resin. The thickness of the composite laminate is 3.5 mm, being the same that Zhuge et al.¹⁶ propose to validate their thermal model, so similar properties have been considered.

Figures 4(a) and 4(b) present mass loss-time and temperature-time profiles respectively, for a heat flux of 50 kW/m^2 at three representative surfaces of the sample (front $x = 0 \text{ mm}$, middle $x = 1.75 \text{ mm}$ and back $x = 3.5 \text{ mm}$). We have included in the graphics a numerical average curve (100 integration points through thickness) and experimental data measured by Zhuge et al.¹⁶ to probe the very good agreement with our numerical results.

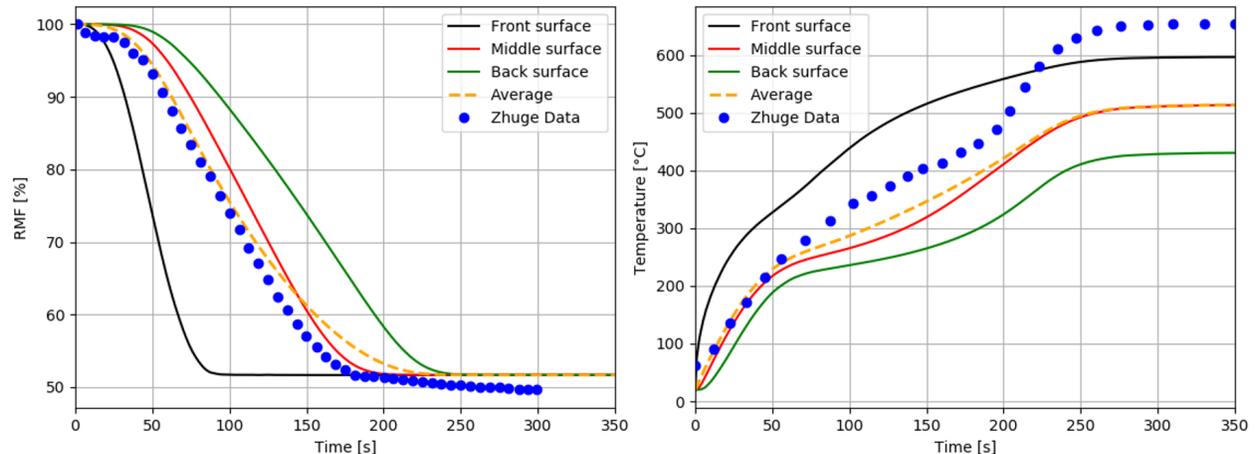


Fig. 4 (a) RMF profiles and (b) Temperature profiles. Comparison between our numerical simulation prediction and experimental data of Zhuge et al.¹⁶ for an E-Glass/polyester laminate submitted to a heat flux of 50 kW/m^2

Figure 4(a) represents the amount of matrix that is thermally decomposed when the laminate is exposed to a constant heat flux. As the matrix decomposes, it releases volatile substances that reduce the mass of the laminate. As the decomposition rate of the matrix increases, it releases volatile gases at a faster rate (Heat Release Rate, HRR), which is measured by an increase in the rate of mass loss. The kinetics of mass loss is relatively fast for a heat flux of 50 kW/m^2 , because of high enough temperature, which reaches its stationary value in 300 seconds approximately. The laminate is heated to a maximum temperature of about 600°C on the upper front surface and at a minimum temperature of about 425°C on the lower back surface, as shown in Fig. 4(b). That is a consequence of the thermal conductivity decrease and also of the porosity creation and increase during the material degradation.⁹

Comparing Fig. 4(a) and Fig. 4(b), mass loss begins at the frontal surface from a temperature of about 300°C , which means that the vinyl ester matrix does not decompose below this temperature. A decomposition gradient of the matrix is observed as a function of the exposure time and the through-thickness coordinate, so that the decomposition is slower when one moves away from the frontal surface directly in contact with the radiative hot source.

These results are in very good agreement with the measured values from the literature,¹⁶ so that lets trust in the thermal model to predict thermal behavior of polymer composite laminates exposed to an unidirectional constant heat flux. Moreover, thermal model allows evaluating others variables that are not available with typical thermal model presented in the literature,^{6,7,8,16} such as thermal expansion, density, gas flow rate, gas mass storage, permeability, porosity volume fraction, and internal pressure rise, but they are hardly comparable with experimental data, due to difficulty of measurement of these parameters in experimental tests.

Numerical results have been obtained for the same laminate using the hygro-thermal model presented in Section II.B, for a heat flux of 50 kW/m^2 . Figures 5(a) and 5(b) present mass loss-time and temperature-time profiles respectively, with an initial water mass fraction content of 5% related to the solid mass of the laminate. A first step of mass loss is observed due to the material desorption from about 100°C (water vaporization temperature), followed by a second decrease of mass, due to the decomposition of the matrix by pyrolysis. Numerical average curves (orange discontinued lines) are confronted against average curves (purple discontinued lines) from the previous thermal model results presented in 4(a) in order to analyze the influence of water content.

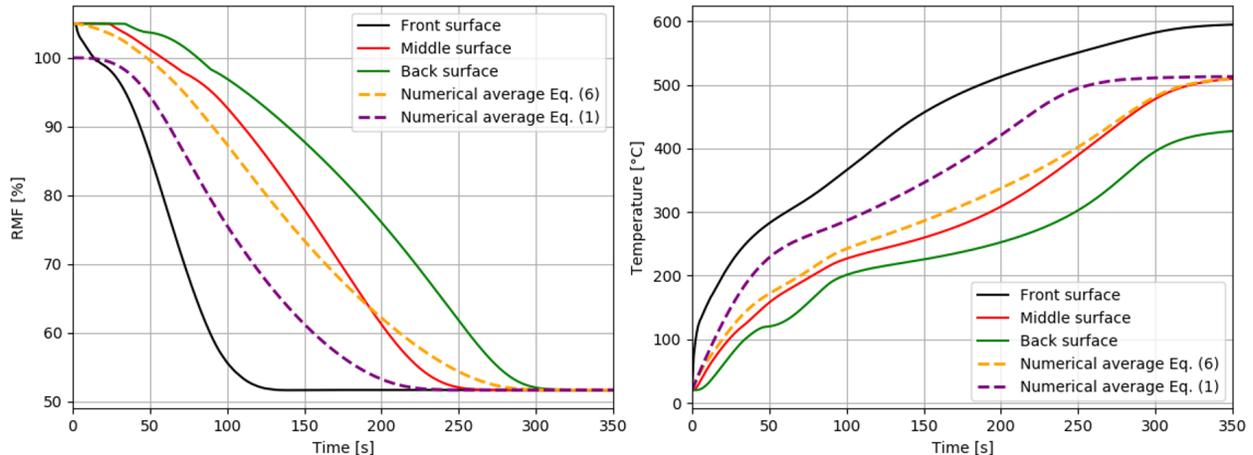


Fig. 5 (a) RMF profiles and (b) Temperature profiles. Comparison of numerical simulation between thermal and hygro-thermal models for a 3.5 mm thickness E-Glass/polyester laminate submitted to a heat flux of 50 kW/m^2

Figure 5(a) shows that matrix degradation is clearly slower in the wet sample, because of coupling between water desorption and pyrolysis reaction, whose kinetics are different. Consequently, evolution of $T(x, t)$ is also slower, particularly at first step, due to consumption of a part of the heat flux energy to produce the water evaporation process. Thus, our model is able to predict the hygro-thermal behavior of polymer composite materials through a relatively simple approach, taking into account the evolution of water content through the material thickness as an additional variable of the thermal problem. In an analogous way, it is valid to predict the hygro-thermal response of sandwich composites with polymer laminated skins and combustible core, following the approach exposed in Section II.C.

In the case of wet sandwich thermal degradation, the model calculates the instantaneous temperature $T(x, t)$ for each abscissa x in the thickness direction of the sandwich, which evolves differently depending of thermal properties of each constituent of the sandwich sample. Thus, mass loss is a consequence of progressive mass loss of each component of the sandwich material, taking into account the water content inside each one. That can be numerically observed thanks to kinetics of water content and mass loss for each constituent, which can be analyzed in more detail from the $m_{\text{H}_2\text{O}}(x, t)$, $\text{RMF}(x, t)$ and the mass loss coefficient $\alpha(x, t)$ for any through-thickness coordinate. E-glass/polyester (or vinyl ester)/balsa samples have been evaluated, but results are not presented in this Section.

Coherent results using hygro-thermal model have been obtained for both laminates and sandwiches, which justifies assumptions done in Section II.B and II.C to formulate it. However, an experimental validation at laboratory house is envisaged to contrast numerical predictions in moisture and temperature conditions. Moreover, other conditions (different heat flux, fiber/matrix rate or laminate/core thickness) can be evaluated, predicted and compared with the presented models, but this study is not presented in the present paper.

B. Hygro-thermo-mechanical durability

The temperature and mass loss profile predictions obtained in previous Section III.A, are used as input to calculate the post-combustion mechanical properties of composite materials. The CAF can be calculated for different rate of decomposition, supposing that the material reaches progressively a certain value of $\alpha(x, t)$ at each surface through the thickness direction. Then, we can calculate the normalized flexion modulus using Eqs. 10 and Eq. 12 for laminates or sandwiches respectively. Figure 6(a) shows CAF for a degradation rate of 50% corresponding to $\alpha(x, t) = 0.5$ (intermediate decomposition), and Figure 6(b) shows NFM, for a 3.5 mm thickness E-Glass/polyester composite laminate, exposed to an unidirectional heat flux of 50 kW/m^2 . Numerical results are superposed for a dry material and a wet material having an initial water mass fraction content of 5%. Experimental measured data obtained by Zhuge et al.¹⁶ are also included in Fig. 6(b) for a better comparison.

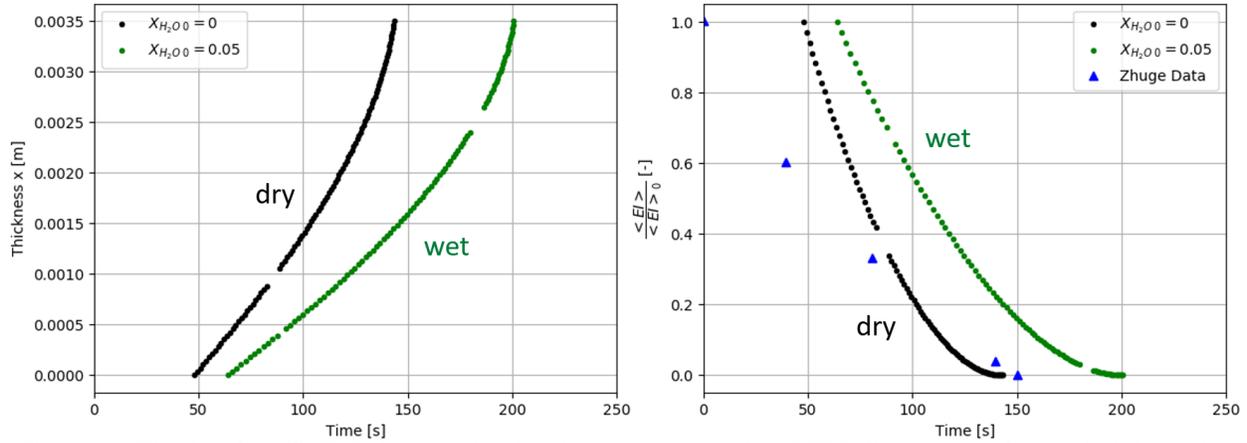


Fig. 6 (a) Kinetics of the CAF. (b) Post-combustion time dependence of the NFM. Comparison of numerical simulation prediction for a degradation rate of 50% between pure thermal and hydro-thermal models

It is observed in Fig. 6(b) that the fall of the FM depends directly on the time of exposure to fire. In fact, combustion time is related to the position of the CAF as shown in Fig. 6(a): over time, the thickness of the carbonized layer increases, as well as its contribution to the overall properties of the composite laminate. Low differences are obtained between numerical results and experimental data for the dry sample at first time, as a consequence of assumption to define the CAF for an intermediate state of decomposition, while NFM begins to be reduced from the starting of the decomposition of front region, even before if we consider a change of the material behavior or possible damage problems.¹⁷ However, the agreement of the curve considering a degradation rate $\alpha(x, t) = 0.5$ with experimental data is enough good to validate the present approach for the prediction of mechanical PC properties in polymer composite materials, and it makes it possible to use it for wet samples. Water content modifies the thermal answer during the combustion, and therefore, post-fire mechanical properties are directly influenced by water content. One could observe in Fig. 6(a) and Fig. 6(b) that CAF and the NFM in the case of the wet material are both offset in time respect to the predictions obtained for the dry material. This effect is due to the evaporation process of water, as it could obviously be predicted from the thermal degradation and temperature results shown in Fig. 5. The fact of having a certain amount of water contained in the material will induce a *thermal barrier* effect, which will slow down the evolution of temperature, and therefore the advance of the combustion front, slowing down the decrease in mechanical properties of the laminate.

Thus, this approach can be also used for estimation of PC properties of sandwich samples, supposing some additional considerations. In fact, only front skin must be considered, because failure of sandwich is assumed to occur by unstable micro-buckling (kinking) of the front skin.¹⁴ That is also observed in experimental data of FM obtained from three point bending flexural tests, on thermal aged samples at different combustion time.¹² Front skin is submitted to compressive stress and has the highest degradation rate, what produces its failure at a first point. Then, the others sections of sandwich sample; balsa core and back skin are assumed to suddenly collapse because they are not capable to support the bending state initially supported by the whole sandwich structure. We note that the strength of the core is assumed to be much lower than the strength of the skins, so its contribution can be neglected. Thus, as the front skin degradation progresses and finally collapses, the back skin must support practically all bending load, which produces its sudden failure.

Numerical results have been obtained for a sandwich material consists of glass/polyester skins surrounded a balsa wood core. Skins are made of superposed layers of M450 (fiberglass chopped strand mat), Soric2, QX868 (quadraxial (0°/-45°/90°/+45°) E-Glass draped layer) embedded in polyester resin.¹¹ The total fiber volume content is 30%. The upper and lower skins thicknesses are 3 mm each one, embracing the 14 mm balsa core thickness. The overall dimensions of the tested sandwich composite specimen are 40 x 40 x 20 mm³. Material data of E-Glass/polyester skins is similar to those presented for the analogous laminate previously exposed, while balsa properties can be consulted in the literature.¹⁴

Initial porosity of virgin balsa core has been estimated of around 30% of volume fraction, while initial porosity of balsa section of sandwich sample is lightly lower, around 25%. Thus, we have considered a 5% of volume fraction of polyester resin diffused inside the balsa core. Figure 7(a) shows the RMF (left axe) and the CAF (right axe) of E-glass/polyester/balsa sandwich composite exposed to an unidirectional heat flux of 50 kW/m². It is defined for a degradation rate of 50% for each constituent of the sandwich sample, corresponding to $\alpha(x, t) = 0.5$ for each one (intermediate decomposition). Figure 7(b) shows the EFM, using Eq. 12 only considering the contribution of front skin, as explained above. Numerical results are superposed for a dry material and a wet material having an initial water mass fraction content of 20% related to porosities of the balsa core. Experimental measured data from laboratory presented by Legrand et al.¹² are superposed in Fig. 7 to make be possible an appropriate comparison with our numerical results:

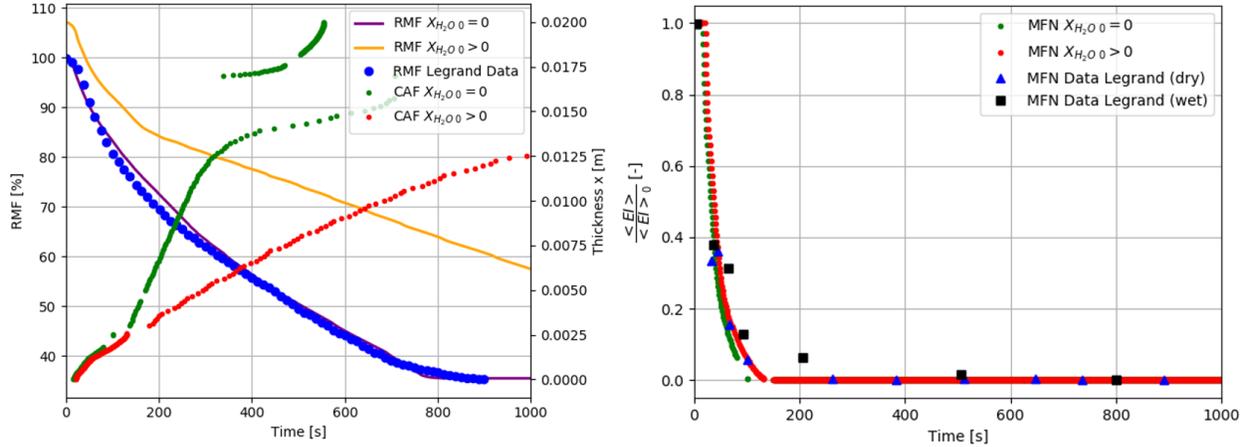


Fig. 7 (a) RMF and CAF. (b) EFM. Comparison of numerical simulation for a degradation rate of 50% between pure thermal and hygro-thermal models for an E-glass/polyester/balsa sandwich composite submitted to a heat flux of 50 kW/m²

A good agreement between numerical results and experimental data is obtained for a dry sample. In addition, we observe that degradation is considerably affected by water content. Differences are more remarkable in balsa core section and back skin, because the mainly amount of water is placed inside balsa core, reducing progressively thermal gradients in the through-thickness direction because of less remaining heat flux energy as a consequence of consumption of energy by the evaporation process, which retards the CAF as shown in Fig. 7(a). On the other hand, EFM in the case of the wet material is slightly offset in time respect to the prediction and experimental data obtained for the dry material (7(b)), being a difference not as marker as that observed in Fig. 7(a) for the RMF and CAF. That is a consequence of definition of real equivalent flexural modulus, which corresponds to normalized flexural modulus of front skin, whose thermal degradation is influenced by residual water content inside initial porosity of the front skin matrix and water vapor flow produced by evaporation of water content inside the balsa core, which might slightly cold the front surface. However, these little differences can be important, and they can be estimated from the thermal degradation results.

As a consequence of agreement of our numerical results with experimental data, we can validate the hygro-thermal model presented here, which allows to accurately predict PC mechanical properties for both polymer laminated and sandwich composites with combustible core, in high temperature conditions and moisture environments.

IV. Conclusion

Fire thermal response and decomposition of polymer composites depend of several parameters that are strongly coupled between each other. A numerical 1D thermal model has been developed considering the main phenomena concerning exposition to fire of composite materials in severe environment.

The model presented concerns a first approach to predict materials hygro-thermo-chemico-mechanical durability for both fiber-reinforced polymer laminates and sandwiches with polymer laminated skins and combustible core in extreme condition of temperature and moisture, allowing the variation understanding of a large numbers of parameters, such as temperature, mass loss, thermal expansion, density, gas flow rate, gas mass storage, permeability, porosity, volume fraction, internal pressure, moisture content, combustion advancing front, and leading to the prediction of the material post-combustion mechanical properties. This is the first step to evaluate the behavior of composite materials from a more realistic point of view, which becomes important to assessing the material behavior at the microscopic scale.

Some aspect can be easily implemented in our model, such as more complex degradation kinetics in several steps of matrix and even of fibers, whose degradation must be modeled in case of application of a high heat flux. Mechanical properties are directly dependent of the thermal answer, it is observed that the fall of the flexural modulus depends directly on the time of exposure to fire, advancing the position of the CAF and consequently, increasing the long of the carbonized layer and the contribution of char material to the overall mechanical properties, so it is envisaged to include explicitly mechanical aspects such as debonding matrix-fiber, matrix cracking, ply delamination or progressive failure ply by ply by stable plastic kinking, what implies the development of model to consider locally effects of progressive damage at the ply scale.¹⁴ Flame evolution is also coupled with thermal degradation, so its modeling could improve the thermal response.¹⁸ In addition, thermal properties have been defined as homogeneous laws, but they could be defined more precisely at ply scale or even at components scale as a function of temperature and degradation rate.

Despite of required improvement, the obtained results are very encouraging and the agreement with experimental data allows to validate the present hygro-thermal model and the approach for estimate mechanical post-combustion

properties. It enables to predict the fire response of laminates and sandwiches at the macroscopic scale (post-combustion properties), from the local through-thickness results of temperature and degradation.

That lets to estimate post-combustion properties of other similar laminates or sandwich specimens, for example a sandwich consisting of 30 mm thickness balsa wood core embraced by 5 mm glass/vinyl ester skins. Fig. 8(a) shows combustion advancing front defined for a degradation rate of 50%, and Fig. 8(b) shows equivalent flexural modulus for a heat flux of 50 kW/m^2 . Numerical results are superposed for a dry material and a wet material having an initial water mass fraction content of 20% related to the porosity volume fraction of the balsa core section, in order to compare them, and an analogue effect of water content can be observed respect to the previous calculated results for an E-glass/polyester/balsa sandwich composite (Fig. 7).

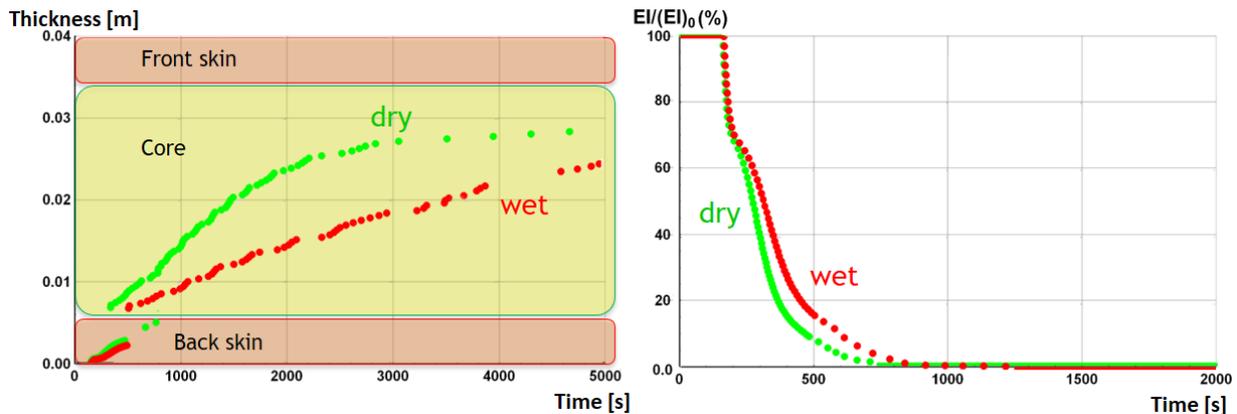


Fig. 8 (a) CAF. (b) EFM. Comparison of numerical simulation prediction for a degradation rate of 50% between pure thermal and hygro-thermal models for an E-glass/vinyl ester/balsa sandwich submitted to a heat flux of 50 kW/m^2

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