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Modelling Reaction-to-fire of Polymer-based Composite Laminate

Damien M. Marquis and Éric Guillaume
Laboratoire national de métrologie et d'essais (LNE)
France

1. Introduction

The use of polymer based laminate composite has greatly increased in the last 20 years. These materials offer many advantages in engineering applications. However, unlike other materials such as steel and aluminium, current composites materials commonly used in structure are reactive. They decompose and release heat and smoke when exposed to high temperature fires. The diverse range of uses for composite materials shows that they can be exposed to a variety of fire threats. In some cases, this use can increase the risk or the likelihood of severity. Several case studies of fire in aircrafts and ships have demonstrated the importance of understanding the fire reaction of composite.

The knowledge of the fire behaviour of polymer composite material is of great importance from a practical point of view because of their widespread use in several domains (aircraft, shipbuilding, railways,etc.). The fire behaviour of a diverse variety of composite material has been analyzed since the 1970s. Usually, it is defined by their *fire reaction* and *fire resistance* [ISO13943 (2001)]. Fire reaction is described as "*the response of a material in contributing by its own decomposition to a fire to which it is exposed under specified conditions*". Fire resistance is defined as "*the ability of an item to fulfil for a stated period of time the required stability and/or integrity and/or thermal insulation, and/or other expected duty specified in a standard fire-resistance test*" .

The aim of this chapter is to give a global point of view on the modelling reaction-to-fire of polymer-based composite. It defines the elements of knowledge and the parameters for the characterization of these materials and the modelling of various processes related to combustion. This chapter will describe how heating up a composite material leads to flaming ignition up to surface fire growth. The discussion will be focused on composite material with fuel polymer matrix (thermoplastic and thermoset resin) reinforced with non-combustible fibres (carbon or glass). Special attention is given by Mouritz & Gibson (2006) on fire behaviour of thermoplastic and thermoset matrix, consequently this part is not treated in this chapter. The reaction-to-fire of polymer matrix can be synthetically divided into five (major) parameters, as shown on Fig 1 that are heating, decomposition, ignition, combustion, and surface flame spread. The combustion mechanisms, thermochemistry thermodynamics and dynamics of fire are more complex, and are beyond the scope of this chapter. The topic of fire and flame is reviewed in several extensive overviews [Drysdale (1998), Quintiere (2006)]. The main focus of the present chapter is to help the reader to understand phenomena assumptions and simplification embedded in different models and tests that attempt to predict thermal

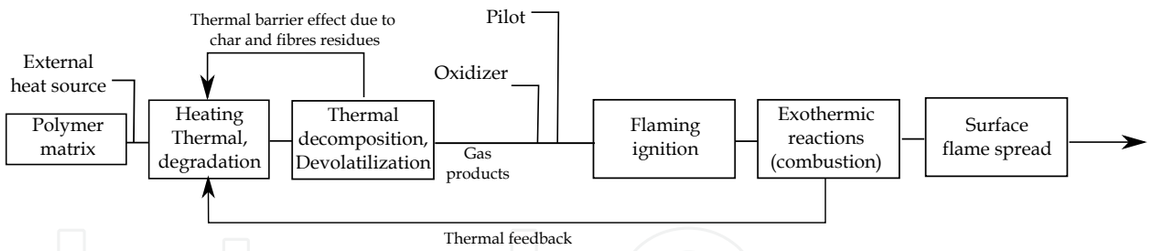

Fig. 1. Reaction-to-fire processes of polymer matrix.

decomposition, ignition, combustion and surface flame spread. All processes involved will be divided in two parts: those associated with the solid phase and those associated with the gas phase.

2. Thermal, physical and chemical processes in solid phase

The devolatilization process depending on thermal decomposition results from exposure to heat and depends strongly on the oxygen content. In an oxidizing flow environment, for example, it is instead the first step of the flaming combustion process, which is defined by a complex physico-chemical process of oxidation, which is accompanied by a release of energy and gas. The devolatilization process of the solid phase of a polymeric material in general and of composite material in particular is a complex and heterogeneous process consisting of several partial reactions. It involves reaction pathway to extensive and irreversible chemical and physical changes caused by heat. This process has been studied since the end of the 19th century by chemists with works on heterogeneous reactions in applications other than fire. The interest of scientists and fire researchers in the problem of how a solid potentially becomes a fuel gas is particularly motivated by the need to quantify the heat and gases source term in numerical simulations and by the increase of calculation capacities. The accurate prediction of the source term can only be attained by the very precise knowledge of the physics and chemistry of the decomposition process. It other words, the pyrolysis products are combustible compounds with high chemical energy that are converted into heat in the flame region. Thus, the prediction of the fire growth requires the quantification of the dynamics of the solid fuel.

2.1 Terminology

Phenomena occurring during "*devolatilization*" are of primary interest in fire safety engineering since the rate of thermal decomposition controls fire growth, spread velocity, release of toxic gases, dripping, production of liquid by products, fire propagation, etc. Thermal degradation and thermal decomposition are different concepts, although these two terms are often considered as synonyms in the literature. Thermal decomposition concerns "*the changes in the chemical structure caused by heat*". Thermal degradation is "*a process whereby the action of heat or elevated temperature on a material, product, or assembly causes a loss of physical, mechanical, or electrical properties*" [ASTM (E176)]. Thermal degradation is mostly related to materials applications. Changes in thermal properties with temperature highly influences the heat transfer into the solid and the heat and mass transfer towards environment.

The behaviour of a previously defined composite material strongly depends on the environment and more particularly on the oxygen content. So, according to the O_2 concentration, it is possible to separate thermal decomposition by *thermolysis* and those

by *thermo-oxidative decomposition*. Etymologically, thermolysis is composed of Greek roots "*thermo*", denoting the temperature, and "*lysis*", derivative of "*lusis*" which defines the loss or disintegration. Therefore, thermolysis defines the thermal decomposition of a polymer under the effect of heat only. The scientific community used the thermolysis decomposition when the process occurs in the absence of oxygen. It uses the term *thermo-oxidative decomposition* when the devolatilization process results from the combined effects of heat and oxygen. In a more global way, the term "*pyrolysis*" translates the decomposition under the action of a fire. During combustion, oxygen is lacking and it is often difficult to separate the processes of thermolysis from those related to oxidation because of their overlapping nature. In the remainder of this chapter, the term pyrolysis is used whatever the environment (oxidizer or inert) to describe thermal decomposition in a fire is.

2.2 Heating up

Consider a "semi-infinite" composite material initially at temperature T_0. It is exposed to an external radiative heat flux $\dot{q}_i''|_{x=0}$ on one face at $x = 0$ as shown on Fig. 2. This moment is defined as the onset of the decomposition process $t = 0$. Heating of the composite material is caused either by an external heat source, or when combustion is initiated by the exothermicity of reaction (thermal feedback). In the solid phase, a heat wave δ_t move up in-depth mainly by thermal conduction phenomena $\dot{q}_c''$ from the sample surface where the heat is absorbed. Heat conduction is a transport phenomenon of internal energy due to heterogeneity of molecular agitation. The highest temperatures are reached close to the surface, and in-depth energy transfer by conduction and radiation will result in an increase in temperature of the deeper parts of the slab. The temperature $T(x,t)$ vary in depth and in time. Thermal degradation leads to a significant variation of thermophysical properties in-depth and in time. The radiative absorption $\kappa(x,t)$ in-depth depends on the intrinsic characteristics of composite material (opacity, etc.). Progressively, a series of physical and chemical processes are initiated as the energy reaches the composite surface.

2.3 Thermal decomposition

In their reference paper, Hirschler & Morgan (2008) explain these phenomena. The authors explain that the nature of the volatile products of thermal decomposition is dictated by the chemical and physical processes and their interactions.

2.3.1 Chemical processes

In the absence of oxygen, a solid polymer experiences a physical degradation and a chemical decomposition when it is subjected to a heat source. At a low temperature ($t \sim 100°C$), it undergoes no chemical decomposition but a thermal degradation. Furthermore, it can release residual monomers depending of the initial product and or the additives. The chemical decomposition and devolatilization appears beyond a certain temperature, called *temperature of decomposition*. In a general way, the literature shows that the thermal decomposition of a polymer is an endothermic phenomenon, which occurs before the flaming ignition, in an interval of temperature bordered between 200 and 400°C. Beyond the decomposition temperature, i.e. when the energy contribution is increased to bond dissociation energy of macromolecules, an irreversible change begins. The thermal decomposition of a polymer is often initiated by the dissociation of chemical bond (covalent bond) to form radicals. Bond dissociation energy depends on the nature of the atom making up the bond and also of the

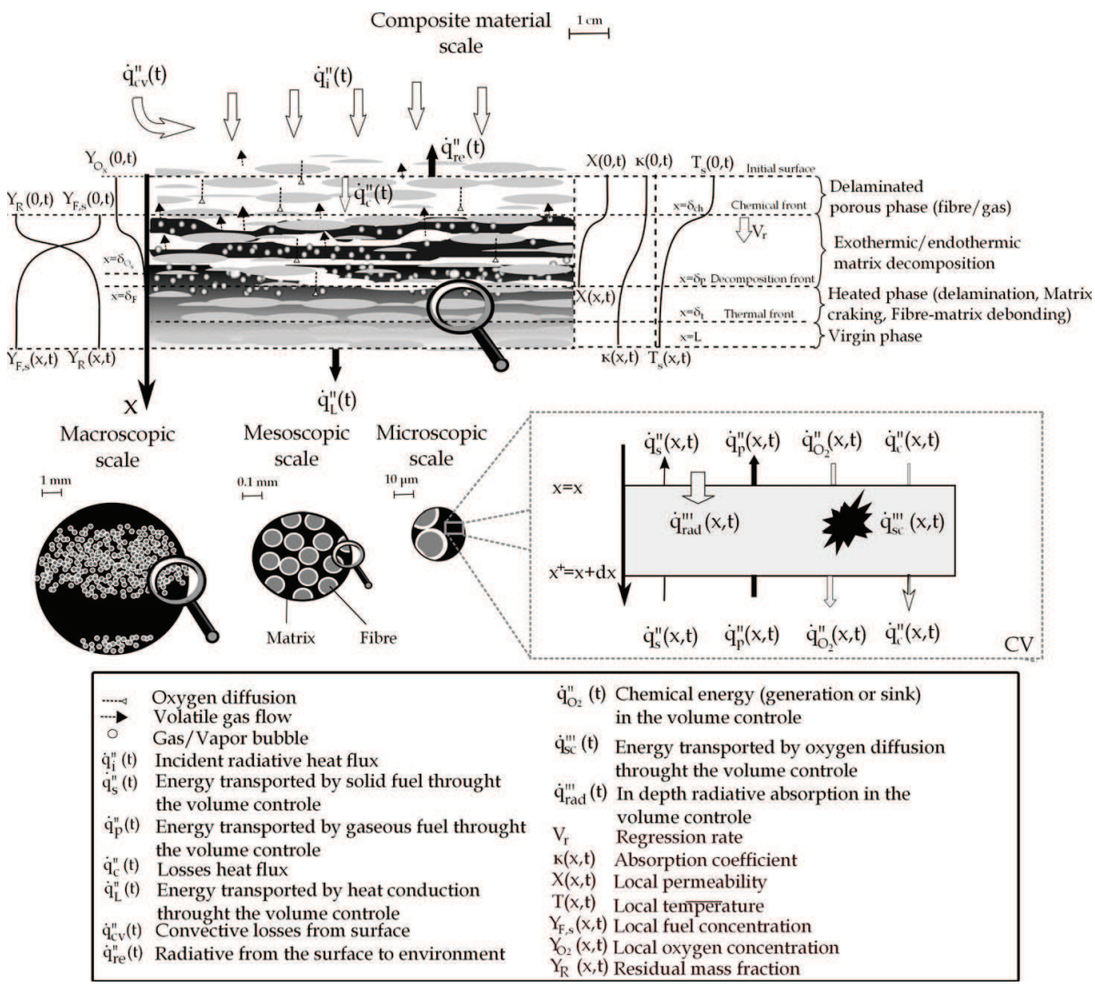

Fig. 2. Schematic of the reaction processes in the through thickness direction of a decomposing polymer composite prior to ignition induced by an external radiant heat source. Several scales of observation of a polymer reinforced fibres composites laminate. Volume control (VC) showing the main heat transfer mechanism in the composite material.

structure environment in which the bond occurs. This endothermic process, more collectively called "*thermal cracking*", results from the thermal excitement of atoms and depends naturally on the temperature and on the presence or not of oxygen. This phenomenon is random but depends on a macro-molecular chain. Four general mechanisms are important for the thermal decomposition of polymer matrix [Troitzsch (2004)] : (1) random chain-scission, in which the polymer backbone is randomly split into smaller fragments; (2) chain-end scission, called *unzipping*, in which the polymer depolymerises from the chain-ends; (3) elimination of pendant groups without breaking of the backbone; and (4) cross linking. In fact, only a few polymers decompose predominantly through one mechanism. Indeed, in many cases a combination of two or more mechanisms can coexist even if generally one of them prevails [Vovelle & Delfau (2000)]. The dominant reaction is generally the random chain scission. Matrix polymers that decompose by random scission and depolymerization are usually more flammable than polymers that cross-link or remove than groups.

As opposed to the thermal decomposition by anaerobic thermolysis, the thermo-oxidative decomposition occurs in the presence of oxygen. Bolland & Gee (1946) have tried to understand the phenomenon by studying the thermal-oxidation of polyolefin and rubbers. The mechanism they have developed could be applied successfully to a large number of polymers such as a polymer matrix of composite materials. The decomposition process is accelerated by an oxidant (such as air or oxygen). In a composite, the oxidative process occurs generally at the surface region. The low permeability of the composite and devolatilization from the decomposition zone impedes the ability of oxygen to diffuse into the condensed phase. Atmospheric oxygen does not have of a major influence on the process of in-depth decomposition because the front moves deep into the condensed phase. Therefore, decomposition tends to be driven in-depth only by the heat. The oxidation process leads on surface to the formation of a continuous "crust", whose thickness increases temporally to an asymptotic value. The position of this asymptote does not vary much with the temperature or the nature of the polymer matrix. In this layer called "*char*", the concentration of the products of oxidation is maximal on the surface and decreases gradually within the polymer. The formation of this layer can be accompanied by the appearance of superficial cracks, which is then deported to the decomposition process into a solid.
Devolatilization processes lead to the formation of gas fuel and toxic and corrosive volatile species (generally with aliphatic and aromatic hydrocarbons light as well as oxygenated compounds). The gas mixture with an oxidizer can be at the origin of the flaming ignition. This phenomenon will be detailed in this chapter.

2.3.2 Physical processes

2.3.2.1 Polymer matrix decomposition

The physical processes of laminate and sandwich composite in fire has been a topic of intensive investigation in recent years. A complete review is given by Mouritz & Gibson (2006) and Hirschler & Morgan (2008). The heating of a laminate composite is led by the surface irradiance level and the thermal diffusivity of the virgin material. The thermal diffusivity of the laminate is particularly low in the thickness direction because of the thermophysical properties of fibres. Thermal diffusion causes a degree of expansion within the matrix due to the thermo-mechanical strain [Grenier (1998)]. When the surface of a composite material reaches a sufficiently high temperature, the decomposition and devolatilization of the polymer matrix start. Polymer matrix degrades in the sequence of endothermic reaction that usually occurs by chain-scission depending on composition. Volatiles resulting from this scission have a cooling effect on the laminate as a whole and it results in a contraction of the composite. The pressure exerted by the trapped gases onto the soft complaint matrix can lead to matrix crack delamination, i.e. the separation of fibres plies which depend on the architecture of fibre. It was marked by an audible tearing sound. The delamination causes the formation of an unbounded interface between fibre plies, which produced a significant rise of the thermal resistance (with the presence of a gaseous barrier). The shielding effects of emerging voids can slow down the decomposition rate of the virgin condensed phase.
Before flaming ignition can occur, fuel polymer matrix needs to be transformed in the gas phase. Reaction rates associated with thermal decomposition can be considered negligible up to the decomposition temperature and therefore, the composite material will not undergo any chemical transformation but can have some physical changes. As the temperature increases,

reaction rates increase and the solid fuel starts changing. Given the temperature distribution within the material, the rates of decomposition are a function of the depth x. Fig. 2 shows a through-thickness view of a composite exposed to one side heating-up in a fire, and the damage is seen to occur in a different zone through the material:

1. the *decomposed porous phase* ($0 < x < \delta_{ch}$), which characterizes the region where the polymer matrix is fully decomposed. This phase composed of fibres and gas, acts as an insulator, inhibiting the heat conduction to the chemical phase ;
2. the *chemical phase* ($\delta_{ch} < x < \delta_p$), which defines the part of the polymer which produces the vast majority of irreversible chemical reaction ;
3. the *heated phase* ($\delta_p < x < \delta_t$), which is the depth to which a solid is heated enough to change its physical properties without deteriorating its chemical properties ;
4. the *condensed phase* ($\delta_t < x < L$), which designates a solid in its virgin state (non-thermally and physically altered).

The mass fraction of flammable gases present in the local productions of decomposition is described with the means of a single variable $Y_{F,s}(x,t)$. This function, which represents a global contribution of all products that can be further oxidized, varies in-depth and in time. It is minimal at the surface $Y_{F,s}(\delta_{ch},t)$. Some composites are highly permeable and allow to transport species in and out the solid. If the pyrolysis rate is small compared to the diffusion of oxygen, oxygen can diffuse in-depth up to $x = \delta_{O_x}$. In-depth oxygen distribution ($Y_{O_x}(x,t)$) reaches ambient values at the surface ($Y_{O_x}(\delta_{ch},t)$). For other composites, oxidation occurs on a small thickness close to the surface. The oxygen and fuel gas concentration are controlled by the permeability of the solid $\chi(x,t)$, the production/comsummation rate and indirectly from temperature distribution $T(x,t)$. Here, the permeability function is a combination of permeability, porosity and any damages that can occur within the composite material.
During the decomposition, the frame of reference $x = \delta_{ch}$ moves with a velocity V_r towards the unexposed surface as the fuel matrix is consumed and the surface regresses. The polymer content is negligible at the surface because the matrix has completely degraded and any residual organic component has condensed into char. The endothermic decomposition of the polymer matrix continues until the reaction zone reaches the rear-face of the laminate. The energy generated by the reaction is now fed back to continue the decomposition process. The gas fuel encounters the ambient oxidizer close to the solid surface and if the condition is sufficient, these gas mixtures can ignite.
All the polymer composites do not break down in a similar way [Drysdale (1998)]. As previously defined, the decomposition process depends on the chemical structure of the specified polymer, in particular on its polymerization degree.
For example, the progressive heating up of certain polymer matrix such as thermoplastic resin or thermoset resin (epoxy, vinylester, polyester) promotes the softening of polymer matrix without any irreversible change, and then the onset of nucleation sites resulting from the break down of molecular chains from the decomposition zone. The devolatilization promotes bubbling that congregate in cavities through this region and diffuse to the surface under the effect of pressure gradients and buoyancy. The presence of gas-phase oxygen reduces the viscosity of the molten polymer matrix, leading to a higher bubbling frequency and a less-violent bursting process. These molecules can escape and undergo further reactions to yield the actual species, usually hydrocarbons and hydroxy radicals, which can lead to a flammable mixture with the oxidizer. The in-depth degradation is going to depend partially,

but not only, on radiative properties of the polymer and more particularly on its emissivity and on its transmissivity. According to the faculty of the radiative property of composite, the reaction can occur in various depths. The holes formed by the bubbles at the surface allow oxidant to penetrate in a small thickness ($\sim 1\ mm$), thereby increasing the depth of the oxygen affect region beyond that, which is possible by diffusion. On the surface, The oxygen diffusion $Y_{O_x}(x,t)$ produces a thermo-oxydative reaction which leads to the formation of a viscous carbon residue [Pal & Mackásy (1991)], commonly called *tar*. This thin oxidized layer δ_{O_x}, strongly affects the process and kinetics of thermal decomposition [Brausman (1988), Kashiwagi (1994)].

Other polymers matrix such as phenolic resin lead to the formation of a solid carbonaceous residue known as *char*. Char is a highly porous material that consists in graphitic and amorphous region. It should be noted here that the proportion of fuel gases and char products depends on the matrix composite and the environment in which the devolatilization takes place (pressure, temperature, oxygen concentration). This char results in random chain scission reactions and cross-linking of the condensed phase. It reduces the heat transfer between the heat source and the virgin condensed phase. This phase limits the reaction rate [Kimoto & Tanaka (2004)]. The amount of char formed in a composite material is dependent on the chemical nature of the polymer matrix and, if present, organic fibres. During the carbonization of the solid, the pressure gradients generate the formation of cracks in the carbon layer. These allow repulsing the gases produced by the decomposition of the solid. Parker (1992), Levchik & Wilkie (2000) specify that these gases are going to cool down by convection of the residues whose temperature is much higher than gas.

The fire condition also has a large influence on the fire behaviour of composite material. Most experimental studies were performed under well-ventilated condition. However, the atmosphere of some fires can be substantially different for example in vitiated condition. In this cases, the lack of oxygen leads to a modification of decomposition by physical (e.g. flame displacement) and chemical (e.g. O_2 diffusion) ways. The temporal evolution of gaseous compounds and decomposition rate of the solid phase are altered by oxygen depletion, such as gaseous species. Hshieh & Beeson (1997) investigated the effect of oxygen concentration in a fire atmosphere on epoxy and phenolic material. It shows that the ignition time decreases slowly with increasing oxygen content and this is because more oxygen is available to react in the flame with the devolatilization products of thermoset matrix. Marquis et al. (2011) have shown for a thermoset-based sandwich composite that when the inlet oxygen level is close to 10 %, the decomposition rate of solid phase is halved compared to the ambient level. The slowest of the mass loss rate with O_2 depletion is the result of the reduction of oxygen diffusion processes in the solid phase. Below 10%, the influences on the decomposition and smoke production are negligible. So, devolatilization is purely a thermolysis process and the solid phase oxidation can then be neglected.

2.3.2.2 Fibre reinforcement

Various types of fibres can be used to reinforce polymer composite, most notably glass, carbon, aramid or less commonly extended chain polyethylene. Other type of reinforcement (bore, polyester, basalt, silica...) can be found but are not considered in this section. In a global way, fibres reinforcements are chemically inert in fire and retain chemical and physical stability at high temperatures. Fibre reinforcement and architecture do not contribute directly to the heat release but they can considerably modify the reaction-to-fire of polymer matrix. Le Bras et al. (1998) have studied the influence of fibre reinforcement on the fire reaction of composite. In

fact, the increase of fibre content reduces the available quantity of fuel matrix in the composite material. Furthermore, it modifies the thermophysical properties of laminate and therefore the heating rate and decomposition rate. The architecture of fibre has also some influence on the thermal behaviour of composite.

The organic agents used as surface treatment of fibres (e.g. to improve adhesion with polymer matrix) are not inert with fire. Fibres are usually covered with a thin layer of organic sizing agent to provide chemical adhesion and specific properties (anti-static, abrasion resistance...). The quantities are very small and the heat release can be negligible compared to the combustion of polymer matrix.

2.3.3 Decomposition rate and reaction pathway of condensed phase.

The decomposition process depends on fuel and heating characteristics, which can distinctively lead to different reaction pathways. The mechanism can be a compendium of reaction that may be sequential or concomitant, and depend on the oxygen concentration. In fact, the thermal decomposition and devolatilization of a heated polymer matrix solid is the net result of hundred of reactions occurring simultaneously [Troitzsch (2004), Mouritz & Gibson (2006)]. Furthermore, exothermic and endothermic reactions can occur simultaneously, which complicates the analysis of thermal behaviour.

Various experimental techniques can be used to study and provide information on chemical reactivity and thermodynamics of a solid polymers matrix in temperature and chemical species. Experimental investigations are generally conducted through thermogravimetry (TG), differential scanning calorimetry (DSC), or differential thermal analysis (DTA). In each case, very small samples are used to reduce heat and mass transfer effects. These analysis of a testing procedure in which mass loss, heat absorption or evolution of the chemical changes of polymer matrix, are recorded as it is dynamically heated inside and over under controlled atmosphere and controlled temperature. It provides qualitative and quantitative information regarding the reaction taking place in a heated solid. Nevertheless, it is often necessary to use a combination of methods to understand the occurring processes. Some simplifications can be defined to hypothesize that the behaviour observed with measurement instruments is caused mainly by the mechanism of decomposition and is not very much influenced by external noise [Bustamante-Valencia (2009), Marquis et al. (2011)].

Generally, these researches are carried out for various heating rates β and two atmospheres (pure nitrogen and air). The basic nature of TG analysis requires an heating rate of 0.1 to 50 $K.min^{-1}$, which is generally slower than typical heating rates in fires (100-150 $K.min^{-1}$). Although these values are much lower than those observed in real fires, they were adopted to clearly separate the reactions. One difficulty associated with using the higher heating rate $\beta \geqslant 50 K.min^{-1}$ in TG is that the thermal lag between the sample temperature and the atmosphere increases with the heating rate, especially if the decomposition process is endothermic. Additional observations performed on the released gaseous compounds can be used to define decomposition mechanisms in accordance with the chemical process [Bustamante-Valencia (2009), Marquis (2010a)]. The measurement of gas release can be performed using a Fourier Transform Infra Red spectroscopy gas analyzer (FTIR) or mass spectroscopy (MS). It allowed the identification of chemical products released by each reaction in the solid phase.

Comprehensive and quantitative mechanisms can be defined using the experimental results coming from the data of the mass loss rate of the condensed phase, the kinetic of release of main gases and the measurement of thermal properties. The approach most commonly

used to describe the decomposition of a solid is not to distinguish the various products of decomposition, but to gather them in "*pseudo-species*" and then group reactions according to their simultaneity. The thermal decomposition of polymer matrix can be implemented in the form of a comprehensible multiple-step reaction pathway with anaerobic thermolysis reactions and oxidation reactions. They are generated based on the hypothesis that each peak of the mass loss rate curves in thermogravimetry represents a reacting species in the solid phase [Ohlemiller (1985), Rein et al. (2006)]. As an example, a reduced comprehensible kinetic mechanisms for polyester resin was found by Marquis et al. (2011), as shown in Table 1. It was defined in accordance with the chemistry of the thermal process. The first reaction

Reactions	Reagents	Condensed products+gas products
Thermolysis	resin	$-v_p$.char+$(1-v_p).[Y_k+Y_j+HCOH+CH_4]$
Oxidation	resin + O_2	$-v_o$.tar+$(1-v_o).[Y_k+Y_j+HCOH+CH_4]$
Oxidation	tar + O_2	$-v_{o,t}$.char+$(1-v_{o,t}).[Y_k+Y_j+HCOH+CH_4+CO+NO+HCl]$
Oxidation	char + O_2	$-v_{o,c}$.ash+$(1-v_{o,c}).[Y_j+CO+NO+HCl]$

$Y_j = CO_2 + H_2O$; $Y_k = CH_3CH_2CHO + C_8H_8$; CO_2 : carbon dioxide; CO : carbon monoxide; H_2O Water; NO: Nitric oxide; HCl: hydrochloric acid; $HCOH$: Formaldehyde; CH_4: methane; CH_3CH_2CHO : Propionaldehyde; C_8H_8: styrene

Table 1. Comprehensible reaction pathway of polyester resin considering species of the solid and gas phases according to Marquis (2010a).

purely encompasses the thermolysis reaction, while the last three reactions include oxidation. Two intermediate products are formed from the initial decomposition of resin polyester, char and tar. The term "*Reagents*" represents the substance that is transformed during the reaction γ. The term "*condensed products*" corresponds to the condensed phase (liquid or solid) that remains in the sample holder at the end of the reaction. Gas effluents, listed in the column "*gas products*", are associated to each reaction γ.

2.3.4 Modelling the thermal decomposition rate

One of the most important factors contributing to the fire hazard of fuel solid composite is its thermal decomposition kinetics. Since the ignition of composite material is usually kinetically controlled, devolatilization is strongly influenced by thermal stability. Although techniques exist for measuring the rate constants of the elementary gas phase, analogous techniques have not been developed yet for kinetics in solid. Nonetheless, some fairly advanced diagnostic tools are used in the field of thermal analysis to investigate the kinetics and thermodynamics of decomposing solids. Since the middle of the 20th century, two main methods have been used to analyze and to model the thermal decomposition of solids in fire applications: the *model-fitting* (modelistic) method and the *isoconvertional* method. The former consists in selecting from a long list of models the one that best fits TG non-isothermal experimental curves. However, this method is applied to single-step reactions and usually various models may lead to indistinguishable fits of experimental data with crucially different Arrhenius parameters [Vyazovkin (2000)]. The latter method was introduced by Kissinger (1957) and improved by Friedman (1963). This method allowed the detection of multi-step decomposition processes, but numerical problems with the temperature integral term were often found. With the improvement of calculation power, a new multi-step decomposition method was proposed by Ohlemiller (1985). Basically, this method consists in predicting the

change of mass in thermogravimetry while the kinetic parameters are calculated by numerical iteration. It is used by several authors [Rein et al. (2006), Matala (2008), Bustamante-Valencia (2009), Lautenberger (2009)] to create a numerical simulation of the decomposition of various materials, and by Marquis (2010a) on composite material.

Traditional methods of parameter estimations from TG data become inefficient or impossible to apply for a multiple-step reaction pathway, such as the one proposed here. The method of parameter estimation employed here is estimated from a mathematical model of the mass fraction equations observed in TG (MLR). A lumped model of the mass fraction processes is developed to simulate transient decomposition during TG experiment according to the above mechanism.

The kinetic model (finished kinetics) is based on the description of thermal decomposition in various stages. Each one of these reactions γ of the comprehensible reaction pathway has an Arrhenius reaction rate $\dot{\omega}_\gamma$ (s^{-1}) defined in Eq. 1.

$$\dot{\omega} = A\, Y_{Ox}^{m}\, Y_{F,s}^{n}\, e^{-E/RT} \tag{1}$$

where Y_F, s is the solid fuel mass fraction, Y_{Ox} is the oxidant mass fraction and the superscript m and n are constants. E is the activation energy ($J.mol^{-1}$), A is the frequency factor or pre-exponential factor (s^{-1}), T is the temperature (K) and R is the universal constant of gases (8,314 $J.K^{-1}.mol^{-1}$). Eq. 1 represents at the moment the most successful model. One shortcoming of using this equation to model the decomposition of thick solids is that the reaction rate within the solid should depend on the local oxygen concentration within the decomposing solid, not only at the surface. However, modelling the penetration of oxygen into a solid to determine the local oxygen concentration is a difficult task. Furthermore, it should be highlighted that there is some debate regarding the interpretation of the kinetic parameter (A E, n and v) as well as the physical trueness of modelling the rate constant using an Arrhenius form. The validity of using the law to treat a heterogeneous reaction has been widely questioned in recent years. In spite of a lot of reactions taking place, these parameters do not have much physical significance. Though the Arrhenius function is often used because it describes the processes remarkably well, the kinetic parameter is nowadays seen as "statistical values". They are dependent of the model and experimental conditions. So, results from two different models are rarely comparable between them (e.g. from the literature). Therefore, it is not illogical to obtain several sets of data for the same reaction.

The mass loss rate (or the time derivatives of mass fraction) of each condensed products j, is expressed as the product of the reaction rate $\dot{\omega}_\gamma$ and the residual mass fraction Y_{R_γ} (where $0 \leq Y_{R_\gamma} \leq 1$).

$$\frac{d}{dt} Y_j = Y_{R_\gamma} \dot{\omega}_\gamma \tag{2}$$

The total mass remaining in the TG sample holder at a time t, [See Eq. 3] can be obtained by summation of the individual condensed products j (solid or liquid) mass losses following Eq. 2.

$$\frac{d}{dt} Y = \sum_{j=1}^{M} \frac{d}{dt} Y_j = \sum_{j=1}^{M} \sum_{\gamma=1}^{N} (Y_{R_{j,\gamma}} - 1) \dot{\omega}_{j,\gamma} \tag{3}$$

The solution to this system of ordinary differential equations requires a stiff numerical solver. The unknowns (kinetic parameters) in the mass balance presented in Eq. 1 are: A_γ, E_γ, n_γ and Y_{R_γ} ($v = 1...N$). The optimum kinetic parameters are the ones that best fit the experimental curves (mass and mass loss rate from TG).

In fact, the current trend for the optimization of kinetic parameters from mass loss rate dY/dt is addressed using an inverse approach, called "*genetic algorithm*"(GA). This indirect method is based on the principles of Darwinian evolution. It is used for the minimization of the differential and integral form of the objective function simultaneously taking into account the difference between the mass-loss model prediction and mass loss measured for all heating rates data. The GA method has lots of advantages such as the ability to treat highly non-linear problems and search spaces that have a high dimensionality [Rein et al. (2006), Houck & Joines (1995)]. However, a major disadvantage of the inverse problems is that the uniqueness of the solution (the kinetic-parameter set) cannot be guaranteed because very complex physical processes are being simulated with a quite simple mass-loss model. For these reasons, an efficient heuristic method, such as genetic algorithms, is therefore necessary, from predefined ranges. The best fitness is obtained in a particular predefined range of input parameters. The uniqueness of the solution is a concern in inverse problem. To resolve the issue, the approach used is to verify that the parameters are applicable at several heating rates. For example, Fig. 3 provides a comparison between the experimental and calculated measurement in nitrogen and air for polyester resin at several heating rates (10, 20 and 50 $K.min^{-1}$).

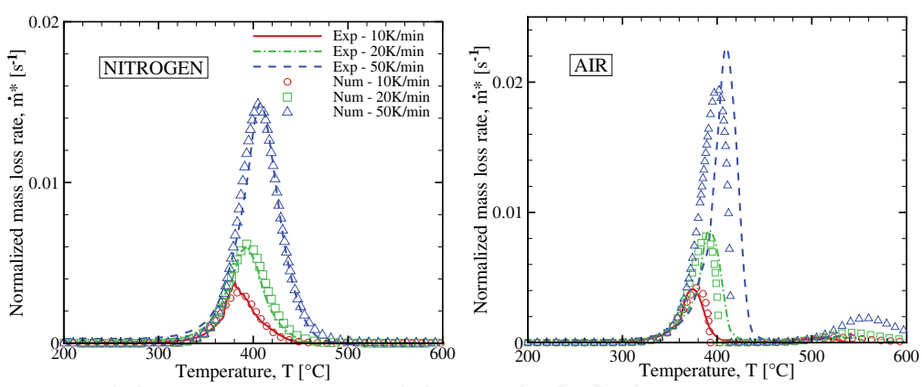

Fig. 3. Solid phase processes of polyester matrix during thermal decomposition for various heating rates β (10, 20 and 50 $K.min^{-1}$) and two atmospheres (Nitrogen and air). a) Plots of mass loss. b) Plots of mass loss rate. [Marquis et al. (2010b)]

An interesting discussion should take place among the scientific community of fire in order answer to the following questions: Is it useful to keep on devoting time and efforts to fit numerically curves by using parameters that do not have a physical meaning and that have a very uncertain application domain? How could the models be improved in order be able to use the experimental results? What is the relevance of these kinetics parameters at another scale?

2.4 Modelling physical transport processes in solid phase during thermal decomposition

Modelling the chemical reaction and transport processes taking place during the thermal decomposition of the polymer solid phase is very difficult because of the lack of knowledge

on physical and chemical processes occurring. Most of the pyrolysis models developed for the polymer and composite material are extensions or modifications of those established for heterogeneous polymers like cellulose, most notably by Kung (1972) and Kansa & Perlee (1977). Many of the processes that occur in burning wood are similar to those described for composite material. Since then, these models have been adapted for modelling the heat and mass transfer through fibre-polymer composite material in fire. Several researchers [Tant et al. (1985), Henderson & Doherty (1987a), Henderson & Wiebelt (1987b), Florio et al. (1989), Sullivan & Salamon (1992a), Sullivan & Salamon (1992b), Perring et al. (1980), Mc Manus & Springer (1992a), Mc Manus & Springer (1992b), Dimitrienko (1995), Davies et al. (1995a)Dimitrienko (1997), Milke & Vizzini (1991), Gibson et al. (1995),Davies & Wang (n.d.), Looyed et al. (1997), Gibson et al. (2004), Lattimer & Ouelette (2006), Trelles & Lattimer (2007)] have developed different approaches but the most influential work in this area came from Henderson et al. (1985). Research on the effects of fire on sandwich composite has used the same principle as single monolithic composite in terms of modelling [Davies et al. (1995a), Davies et al. (1995b), Looyed et al. (2001), Krysl et al. (2004), Galbano et al. (n.d.), Marquis (2010a)]. In all of these cases, some assumptions are made. The main hypothesis is that the thermal decomposition was modelled using a Arrhenius law.

The simplest of these models considers that the pyrolysis occurs at the surface (as it is the case for some thermoplastic polymers) whereas the most detailed considers that it is about a volume, which degrades, taking into account the heat diffusion within the solid matrix. It is particularly the case when we study materials, which generate chars, where gas diffusion processes are important. It is then advisable to characterize the thermal transfers, the oxygen diffusion as well as the degradation kinetics and char formation, which are all relevant parameters. The main difference between the models is that the kinetics of thermal decomposition are considered as infinitely fast. In addition, for reasons of time saving and simplification of calculation, a large majority of these models is based on a kinetic description of pyrolysis, using a single global reaction, but not taking into account all stages of decomposition. The strong nuances between the various mechanisms are the number of reactions proposed, the order of reaction, the number of species within the condensed phase, the description of phenomena and diffusive transport as well as taking into account or not the effective thermal properties of materials. Another limit of these models is not taking into account the influence of oxygen concentration, yet very influential kinetic parameter [Kashiwagi & Ohlemiller (1982), Kashiwagi et al. (1987), Moghtaderi et al. (1996), Dakka et al. (2002)].

Despite these assumptions, models are able to predict a lot a phenomena. Nevertheless, models with a comprehensible treatment of the dynamics of both heat and mass transfer should be developed together with experimental measurements to improve the understanding of the decomposition behaviour of polymer based composite. The next section provide a comprehensible mathematical pyrolysis model for composite materials.

2.4.1 Global comprehensible pyrolysis model

In order to determine the fuel production, it is necessary to define the evolution of the temperature inside the solid fuel. This can be achieved by defining a comprehensive energy equation. The key challenge to the modelling of composite in fire is the complexity of the processes which controls the devolatilization:

- thermal processes (heat conduction, gas diffusion, exo/endothermic reaction, radiation, convection [see Fig. 2]);
- chemical processes (softening, melting, pyrolysis, char formation, oxidation).
- physical processes (thermal expansion, internal pressure build up, vaporization of moisture, delamination damage, matrix cracking, surface ablation and fibres reaction).

Modelling underlies understanding and analysing all these processes as accurately as possible. It is further complicated because many processes are intertwined and do not occur independently of each other. Understanding the way these processes interact is essential to analyse and model the fire behaviour of composite materials.

The study of these phenomena requires knowledge of transfer properties (mass, momentum, energy). As for all the heterogeneous multi-phase systems, these properties obviously depend on the morphology of the matrix and phenomena that develop and interact in the various phases. The approach that is usually used to simulate thermal decomposition is inspired by the works of Whitaker (1977). This one is directly inspired by methods that are traditionally used in continuum mechanics to search for expressions of local conservation laws. The formalism of Whitaker (1977) is based on a "*multiscale homogenization approach*" of the physical equations relative to the microscopic level of each phase (solid matrix, fibre, gas/vapor, moisture) present in the composite material. This approach puts into practice a change of scale, as shown in Fig 2. To simplify the problem, the decomposition process is usually described in a one-dimensional semi-infinite slab with coordinate x for the depth. To determine the pyrolyzate production, it is necessary to solve the evolution of the temperature inside the solid fuel. External radiant heat flux $\dot{q}_i''|_{x=0}$ is applied to the top surface at $x = 0$. The temperature of the solid, initially at temperature T_0, increases as the heat reaches the surface of the slab. In the model formulation that follows, a decomposing material is modelled as consisting of both a condensed phase (resin matrix, char, ash, etc.) and a gas phase (pyrolyzate, oxidant, nitrogen, etc.). Processes in the gas phase, the mixing with the oxidizer and the formation of a flame are not considered. Given the complicated character of the thermal response of a composite material, the mathematical description also uses further assumptions: (1) Pyrolysis kinetics is modeled by a single-step first-order reaction; (2) the composite material forming the skins consists of the volumetric fractions X_f (glass fibres), X_p (polymer), X_m (moisture), and X_g (gas and/or vapours); (3) the effective density of each condensed-phase component of the panel is constant whereas the corresponding volumetric fraction varies to take into account chemical and physical transformations occurring during the exposition to fire; (4) the total volume occupied by each skin does not change as a consequence of thermal decomposition and combustion of the polymeric resin; (5) the solid, liquid and gas/vapour phases are in a local thermal equilibrium; (6) the transport by diffusion of volatile species is small; (7) the transport by convection and diffusion of the liquid-phase moisture is negligible; (8) the gas/vapour mixture obeys to the ideal gas law.

By applying these assumptions and the formalism of Whitaker (1977), the local energy balance on Figure 2 can be reduced to a single equation following the approaches of Kung (1972) and Kansa & Perlee (1977) [Perring et al. (1980), Henderson et al. (1983), Florio et al. (1989), Gibson et al. (2004) Mouritz & Gibson (2006), and Galbano et al. (2009). Estimation of the net heat transfer into a composite material leads to a change in energy accumulation E_{CV} within a control volume CV. [Torero (2008)]. The global comprehensible pyrolysis model can

be summarized by Eq. 4:

$$\begin{aligned}\frac{\partial E_{CV}}{\partial t} = &\left[\dot{q}''_s(x^+,t) + \dot{q}''_p(x^+,t) + \dot{q}''_{O_2}(x,t) + \dot{q}''_c(x,t)\right] \\ &-\left[\dot{q}''_s(x,t) + \dot{q}''_p(x,t) + \dot{q}''_{O_2}(x^+,t) + \dot{q}''_c(x^+,t)\right] \\ &+\dot{q}'''_{rad}(x,t)dx + \dot{q}'''_{sc}(x,t)dx \end{aligned} \tag{4}$$

where $E_{CV} = h_{CV}(x,t)\rho_{CV}(x,t)dx$. h and ρ denote respectively the variation of enthalpy and the density within the control volume. The gaseous species of devolatilization ($\dot{q}''_p$) and oxygen diffusion into the solid ($\dot{q}''_{O_2}$) carry energy in and out the control volume. The mass flow of these gases ($\dot{m}''_p$ and $\dot{m}''_{O_2}$) incorporates the regressions rate. The conductive heat flux is defined in the control volume by ($\dot{q}''_c$). The terms $\dot{q}'''_{rad}$ and $\dot{q}'''_{sc}$ are respectively the in-depth radiative absorption and the chemical energy (generation or sink).

Usually, the considered system consists of a gas phase, a moisture phase, a solid phase (matrix + fibres) and a char. The global comprehensible pyrolysis model takes into account the highly unsteady character of the process, solid and gaseous rise of enthalpy, devolatilization and combustion of the polymeric component of the laminate composite both including finite-rate kinetics, heat transfer by convection and conduction, convective mass transfer, variation of component volumetric fractions, moisture evaporation, surface ablation of the solid residue left after the conversion of the polymeric resin as soon as the temperature reaches a critical value, heat transfer (convection and radiation), and variable properties. Sub-models are developed for the chemical and physical processes with intrinsic values for all the properties. Detailed information about the mathematical description of the various processes and a list of property values are provided below. The unsteady enthalpy conservation equation of the system is written as:

$$\begin{aligned}\frac{\partial}{\partial t}&\left[X_p\rho_p h_p + X_c\rho_c h_c + X_f\rho_f h_f + X_m\rho_m h_m + X_g\rho_g h_g\right] \\ &= \frac{\partial}{\partial x}\left(k_{s,net}\frac{\partial T}{\partial x}\right) - \dot{\omega}'''_m\Delta h_v + \sum_{\gamma=1}^{N}\dot{\omega}'''_\gamma\Delta h_{r_\gamma} \\ &\quad + \frac{\partial}{\partial x}\left[\sum_{j=1}^{M}\dot{m}''_g h_g\right] - \frac{\partial}{\partial x}\left[\dot{m}''_{O_x}h_{O_x}\right] \\ &\quad + \frac{\partial(\rho_s V_r C_{p_s} T)}{\partial x} + \dot{q}'''_{rad}\end{aligned} \tag{5}$$

This equation is coupled with the mass conservation equations and the Darcy equation, becoming a stiff system of differential equations. $X_i(x,t)$ denotes the volume fraction of element i, $k_{i,net}(x,t)$ the thermal conductivity of element i, $C_{p_i}(x,t)$ the specific heat of element i ($W.m^{-1}.K^{-1}$), $\rho_i(x,t)$ the density of the element i ($kg.m^{-3}$), $V_r(t)$ the regression rate of polymer matrix, $\dot{m}''$ the mass flow ($kg.s^{-1}.m^{-2}$), ε the radiative properties of material, h the specific enthalpy ($J.kg^{-1}$), Δh_v the latent heat of water vaporization ($J.kg^{-1}$) and Δh_{r_γ} the heat of reaction γ ($J.kg^{-1}$). Phase changes are incorporated into the heat sinks where some rate function is defined to describe the conversion from one phase to another. The subscripts m, c, f, g, O_x, p and s are used to denote the moisture, the char, the fibres, the gas and vapour,

the oxidizer, the polymer matrix, and the solid respectively.

The boundary condition to the top surface ($x = 0$) is a balance between incoming thermal radiation $\dot{q}_i''$ and heat losses by radiant emission $\dot{q}_{re}''$ and Newtonian cooling $\dot{q}_{cv}''$. It is possible to specify (through the value of the radiative absorption κ for each condensed phase species) whether radiation is absorbed at the surface or in-depth. If $\bar{\kappa}|_{x=0} \neq \infty$, radiation is absorbed volumetrically in-depth. The boundary conditions on the condensed phase energy equation are:
for $x = 0$

$$-k_s \frac{\partial T}{\partial x}\Big|_{x=0^+} = \varepsilon_s \dot{q}_i'' - \varepsilon_s \sigma\big(T^4(0,t) - T_0^4\big) - h_{cv}(t)\big(T(0,t) - T_\infty\big) \qquad (if\ \bar{\kappa}|_{x=0} = \infty) \quad (6)$$

$$-k_s \frac{\partial T}{\partial x}\Big|_{x=0^+} = -\varepsilon_s \sigma\big(T^4(0,t) - T_0^4\big) - h_{cv}(t)\big(T(0,t) - T_\infty\big) \qquad (if\ \bar{\kappa}|_{x=0} \neq \infty) \quad (7)$$

for $x \to L$:

$$0 = -k_s \frac{\partial T}{\partial x}\Big|_{x=L^-} \quad (8)$$

The calculation of the total mass loss rate (sum of the reactions γ) can be evaluated from a local point of view, by the expression [Torero (2008)]:

$$\dot{m}_p'''(x,t) = Y_R(x,t) \sum_{j=1}^{M} \sum_{j\gamma=1}^{N} \dot{\omega}_{j\gamma}''' = Y_R(x,t) \sum_{j=1}^{M} \sum_{j\gamma=1}^{N} \left[A_{j\gamma} Y_{0_x}^{m_{j\gamma}}(x,t) Y_{F,s}^{n_{j\gamma}}(x,t) e^{-E_{j\gamma}/RT(x,t)} \right] \quad (9)$$

It is important to note that fuel produced in-depth does not necessarily reach the surface and, in many cases, that pressure increases within the fuel structure can be observed. The effects of permeability and pressure are combined in a complex manner to define the flow within the composite material. That actually remains an unresolved problem. Furthermore, the use of a simple variable such as χ can be justified to take into account these phenomena. The total fuel production at the surface per unit area can be defined by integrating equation 9 across the thickness L including the permeability function described above:

$$\dot{m}_p''(x,t) = \int_0^L \chi(x,t) \Big[Y_R(x,t) \sum_{j=1}^{M} \sum_{\gamma=1}^{N} \Big(A_{j,\gamma} Y_{0_x}^{m_{j\gamma}}(x,t) Y_{F,s}^{n_{j\gamma}}(x,t) e^{-E_{j\gamma}/RT(x,t)} \Big) \Big] dx \quad (10)$$

where $Y_{F,s}(x,t)$ denotes the local fuel mass fraction, $Y_{Ox}(x,t)$ the local oxidant concentration, $Y_R(x,t)$ the residual fuel fraction, $\chi(x,t)$ is the local permeability, $T(x,t)$ the local temperature and $A_{j\gamma}$, $E_{j\gamma}$, $n_{j\gamma}$ and $m_{j\gamma}$ are the constants kinetics. Throughout this work, the index j is used to denote the condensed product j and the index γ is used to denote the chemical reaction γ.

2.4.2 Thermophysical properties of composites under decomposition

An accurate prediction of thermal decomposition of composite in fire needs to register a large amount of data on the thermo-physical properties of each element constituting the material on the temperature range interest. These properties need to be quantified over the temperatures expected range, which is not easy. For the current simulations, this entails determining the density $\rho_j(T)$, the thermal conductivity $k_j(T)$ and the specific heat capacity $C_{p,j}(T)$ and the gas

permeability χ_j of both virgin condensed-phase species and fully decomposed material, the heats of reaction Δh_{r_γ}, the effective heat of combustion(Δh_c), radiative properties (emissivity ε and absorption coefficient κ) etc. The properties change with temperature and it is necessary to consider the temperature dependence in the analysis.

These properties depend on the weaving style, the characteristic and the density of the different components of other factor introduced during weaving, such as crimp angle, make the prediction very fastidious. In order to achieve the prediction, the conventional method to determine the thermophysical properties of composite material is based on the *multiscale homogenization approach* [Fig 2]. Most methods for modelling the thermophysical properties of composite materials use the concept of homogenization whose purpose will be to link the local thermophysical properties to the global effective thermophysical properties. The large numbers of models vary in mathematic complexity depending on the type of laminate being analyzed. More sophisticated models consider the influence of fibre architecture [Ott (1981)] whereas simple model determine the equivalent thermophysical properties in two direction [Henderson et al. (1985)] : one in the fiber direction called *longitudinal* or *harmonic* and the other perpendicular to the fiber called *transverse* of *Arithmetic*.

The change of thermophysical properties (thermal conductivity and specific heat) in temperature for the laminate and the char is often expressed using empirical curve fit polynomial equations [Mouritz & Gibson (2006)].

$$\phi_v = \phi_0 + \phi_1.T \tag{11}$$

where T is the temperature and ϕ is used to denote the specified property, such as thermal conductivity or specific heat. A complete review is given by Ott (1981), Henderson et al. (1985), Gibson et al. (2004) and Mouritz & Gibson (2006). The temperature dependence of thermal conductivity can also be expressed as a linear combination of the virgin material and char conductivities, weighed by the ratio of the solid material mass to the initial virgin mass or final char density [Henderson et al. (1985)]. These models are not suited for all types of composite material and more complex models are needed to consider the influence of fibre architecture. Furthermore, the prediction capabilities of these models have not been rigorously evaluated, particularly due to the difficulties associated with accurately measuring the temperature dependent thermal conductivity of reagents such as char. It is important to note that the thermal properties of composite may change with the evolution of fire induced damage. For example, the delamination of the virgin phase can reduce the thermal conductivity, slowing the heat transport by creating an air gap between debonded ply layers. Most thermal models ignore this effect of delamination, which leads to an over-estimation of the temperature in the virgin material shielded by the cracks.

In principle, the required properties could be measured with multiple specialized small-scale tests but this approach is not realistic for most practitioners and researchers, due to the expense associated with running multiple specialized tests. For these reasons, Lautenberger (2009) used another approach and estimated the physical properties of condensed phase species from an optimization routine. Nevertheless, some preliminary tests of this code have shown that it costs a lot of time in terms of calculation and generates results that are difficult to interpret. Furthermore, it increases the number of optimized input parameters, which can affect the quality of numerical results, leading to non-physical but mathematical solutions.

2.5 Flaming ignition of laminate composite

The sequence of events leading to the ignition of a gas phase flame is described in this section. It is assumed that gaseous fuel emerges from the heating and the decomposition of the polymer matrix following the description provided in the previous section. The terms of flaming ignition, describe the flame appearance in the immediate neighbourhood vicinity of a polymer. In fact, polymer matrix does not ignite. Only gas burn. To ignite the polymer-based composite, it is necessary to be able to raise the temperature of a composite surface until it exists a volatile flammable mixture of species and oxygen on surface. In other words, the gas pressure must correspond to the lower flammable limit (LFL). If the fuel gas concentration from the surface of the material is insufficient, this ignition results only from a flash point. When the mass flow of product fuel gas is sufficient, a diffusion flame is then established persistently above the material. This condition is not sufficient and flaming requires local contributions of energy. This amount of energy required to start the flaming is called *activation energy*. It depends on the composition and architecture of the composite, pressure and temperature. Since it is made by an external source (flame or electric spark) the ignition is *called piloted*. The ignition can be *spontaneous*, also called *self-ignition*, when energy intake does not result from the exothermic oxidation reactions in the gas phase.

2.5.1 Inert solid assumption

The flaming ignition of a solid fuel in general and of a composite material in particular depends on the ability of heat to diffuse into the solid. To predict flaming ignition, it is necessary to solve the heat equation when it is exposed to a radiant heat flux on the surface. The ignition of polymer and composite material has been successfully modelled using semi-infinite solid heat transfer models, integral heat transfer models and finite difference models. Extensive reviews of these modeling efforts can be found in Kashiwagi (1994), Di Blasi (2000), Moghtaderi (2006), Lautenberger & Fernandez-Pello (2004) and Torero (2008). Consider the composite as a "*homogeneous semi-infinite solid*" initially at temperature T_0. It is exposed to a constant external radiative heat flux $\dot{q}_i''|_{x=0}$ in $x = 0$. For some composite, the velocity of the reference frame V_R is very small and can be assumed to be negligible ($V_r \simeq 0$). Assume that equivalent thermo-physical properties of composite material are considered constants ($\rho_s(x,t) \simeq \overline{\rho}_s$, $k_s(x,t) \simeq \overline{k}_s$, $C_{p,s}(x,t) \simeq \overline{C}_{p,s}$) up to the decomposition temperature and the local permeability is negligible ($\chi \simeq 0$ so $\dot{m}_O'' \sim 0$). However, this assumption is questionable between the degradation temperature ($T \sim 100°C$) and the temperature of thermal decomposition ($T \sim 200°C$). In reality, thermophysical properties vary with temperature but a global set of equivalent properties can be established to give a good estimation of ignition. To simplify the problem, the solid is considered as inert until ignition ($\dot{m}_p'' = 0$). As a result of the assumption, the energy balance is dramatically simplified. Despite the fact that this limitation is not justified, it still is the backbone of all standard test method analyses for ignition. These assumptions allow to reduce the study to a simple problem of one dimension conductive heat flux into the solid. Eq. 5 can be reduced to:

$$\rho_s C_{p,s} \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial x}\left(k_s \frac{\partial T}{\partial x}\right) + \dot{q}_r''' \tag{12}$$

This last term is justified because composite materials are semi-transparent and in-depth radiative absorption is observed. The subscript s define the solid composite. The boundary conditions are given in $x = 0$ by Eq. 6 and 7 in neglecting the term $\dot{q}_i''$, while in $x \to L$, it is

defined by:

$$0 = -k_s \frac{\partial T}{\partial x}\Big|_{x=L^-} + k_L \frac{\partial T_L}{\partial x}\Big|_{x=L^+} \tag{13}$$

where the subscripts L denoted the back face.
If the composite is considered as a solid opaque to radiation whatever the wavelength is, the most of incident irradiance level is absorbed at the surface ($a = \varepsilon = 1$ following the Kirchhoff law where a is the absportivity and ε, the thermal emissivity). Therefore, the in-depth radiative absorption $\dot{q}_r'''$ is negligible in Eq. 12 and the boundary conditions are given by Eq. 6 and 8. This hypothesis is more critical. Small justifications exist in the literature to support these assumptions for composite material. In the case of composite material, the absorptivity (or emissivity) can approach a unit in the visible spectrum.

2.5.2 Thermal behaviour of composite material

One of the critical factors influencing the flaming ignition of combustible materials such as polymer-based composite is the thermal thickness. Actually, the heat wave velocity into the material depends on the thermal effusivity and thickness of the solid. A thin solid can ignite within a very short time when it is exposed to a hot fire because its temperature quickly tends to become uniform due to his weak thermal effusivity. On the other hand, a thick solid is going to tend to heat diffusion by conduction within the condensed phase, which limits the rise of its surface temperature, and consequently its ignition. Consequently, the ignition of a solid is strongly conditioned by its thermal behaviour.
A solid can be defined as *thermally thin* when the thermal wave is absorbed so rapidly that there is no significant temperature gradient (quasi-homogeneous temperature) through it. In contrast, in a *thermally thick* material, a significant thermal gradient exist through the solid. For a homogeneous material exposed to a radiant heat flux, a simple criterion based on the radiant modified Biot number (Bi_r) can be used to establish if the material is thermally thin or thick. $Bi_r = h_r L.k_s^{-1}$ where h_r is the radiative exchange coefficient and k_s the thermal conductivity of the specimen. This approach can however not be used for inhomogeneous material such as the composite material. Another approach is therefore to assess the characteristic depth of thermal diffusion $\delta_t(t)$. It is defined by $\delta_t(t) > A\sqrt{\alpha_s t}$ where α denotes the thermal diffusivity ($m.s^{-2}$). A is a constant (between 1.13 and 4) which evolves from one author to another [Dusimberre (1998), Dembsey & Jacoby (2000)]. This equation is only valid for simple radiative thermal ignition and does not consider heat loss by emission $\dot{q}_{re}''$ which depends on the surface emissivity. This approach considers that a solid is thermally thick if $\delta_t(t)$ does not exceed its sample thickness L (m). In practice this means that most composite material are thermally thin when less than $\sim 1 - 2\,mm$ thick.

2.5.3 Ignition properties

The ignitability of polymer material can be characterized by an empirical parameter, often called improperly "*ignition temperature*" [Simms (1963) Martin (1965)]. This temperature is the lowest temperature at which the surface must be carried to ignite. This parameter is determined through standardized tests or when not using an external energy source. These temperatures depend largely on the size and shape of the specimen, the ambient environment (pressure, concentration of oxygen, ventilation), the heat source, etc. For this reason, the published data relative to the controlled temperature or spontaneous temperature can vary

significantly from one document to another. If the sample is suddenly exposed to an external radiant heat flux, then the time delay between exposure and ignition is named the "*ignition delay time*", t_{ig}. The heating rate directly depends on the "*thermal effusivity*" b of the solid, i.e. its ability to exchange heat energy with its environment. A final link can be made to establish a critical ignition condition. If the ignition delay time is infinitely long, there will be no temperature gradients within the composite material. Surface heat losses will then be equivalent to the external incident heat flux. This represents the minimum heat flux required to achieve T_{ig}, and thus flaming ignition of the solid fuel. This heat flux is named the "*minimum heat flux for ignition*", $\dot{q}''_{min}$. These extrinsic parameters of composite material represent then the entire process of ignition. They can be experimentally measured or defined by theoretical mathematics from the simplifications made in this section. Among the work done on the subject, those of Quintiere & Harkleroad (1985), Delichatsios et al. (1991), Janssens (1993), Hopkins & Quintiere (1996), Moghtaderi et al. (1997), and Tewarson (1995), Spearpoint & Quintiere (2001) and Babrauskas (2003) should be highlighted.

2.5.3.1 Surface temperature

Consider a semi-infinite solid, initially at T_0 and exposed to a radiant heat flux $\dot{q}''_i|_{x=0}$. The surface temperature for a constant property inert solid that is opaque to thermal radiation takes different forms as shown in Table 2 [Lautenberger & Fernandez-Pello (2004)]. These solutions are valid only if the thermophysical properties do not vary with temperature. Although this approximation is usually made, the properties of real composite material generally vary with temperature. The ignition temperature can be evaluated by fixing $x = 0$ and $T(0,t) = T_s = T_{ig}$ when $t = t_{ig}$.

	BOUNDARY CONDITIONS	SOLUTIONS
A	$-k\frac{\partial T}{\partial x}\Big\|_{x=0} = \dot{q}''_i$ $T\Big\|_{x\to\infty} \to T_0$	$T(x,t) = T_0 + \dot{q}''_i \cdot \frac{\delta}{k}\left[\frac{1}{\sqrt{\pi}}.e^{(-x/u)^2} - \frac{x}{u}\mathrm{erfc}\left(\frac{x}{u}\right)\right]$
B	$-k\frac{\partial T}{\partial x}\Big\|_{x=0} = \dot{q}''_i - h_{ig}(T-T_0)$ $T\Big\|_{x\to\infty} \to T_0$	$T(x,t) = T_0 + \frac{\dot{q}''_i}{h_{ig}}\left[\mathrm{erfc}\left(\frac{x}{u}\right) - \mathrm{e}^{\left[\frac{x}{k/h_{ig}} + \frac{t}{t_c}\right]}\mathrm{erfc}\left(\frac{x}{u} + \sqrt{\frac{t}{t_c}}\right)\right]$
C	$-k\frac{\partial T}{\partial x}\Big\|_{x=0} = \dot{q}''_i$ $\frac{\partial T}{\partial x}\Big\|_{x=L} = 0$	$T(x,t) = T_0 + \frac{\dot{q}''_i}{u/k}\sum_{n=0}^{\infty}\left[\mathrm{ierfc}\left(\frac{2n+x/L}{u/L}\right) + \mathrm{ierfc}\left(\frac{2(n+1)-x/L}{u/L}\right)\right]$
D	$-k\frac{\partial T}{\partial x}\Big\|_{x=0} = \dot{q}''_i - h_{ig}(T-T_0)$ $\frac{\partial T}{\partial x}\Big\|_{x=L} = 0$	$T(x,t) = T_0 + \frac{\dot{q}''_i}{h_{ig}}\left[1 - \sum_{n=1}^{\infty}\left(\frac{4\sin(\lambda_n L)}{2\lambda_n L + sin(2\lambda_n L)}\cos(\lambda_n(L-x))e^{\left(-\frac{k}{\rho c}\lambda_n^2 t\right)}\right)\right]$

where $u = \sqrt{4\alpha t}$, $t_c = \frac{k\rho c}{h_{ig}^2}$ and $\mathrm{ierfc}(x) = \frac{e^{-x^2}}{\sqrt{\pi}} - x.\mathrm{erfc}(x)$

A : Semi-infinite solid exposed to a net radiant heat flux (no surface heat losses).

B : Semi-infinite solid exposed to a net radiant heat flux with surface heat losses by convection on the surface (the radiative heat losses are linearized into the convective term h_{ig}).

C : Solid of thickness L exposed to a net radiant heat flux (no surface losses) and perfectly insulated at back face.

D : Solid of thickness L exposed to a net radiant heat flux with surface heat losses by convection (the radiative heat losses are linearized into the convective term h_{ig}).

Table 2. Solutions of the heat equation

2.5.3.2 Ignition delay time

Ignition delay times are generally estimated experimentally because of the difficulty in modelling the ignition mechanism of composite material. Although all these theories have been proposed for calculating the time-to-ignition for combustibles materials, they have never been validated for polymer-based composite. It is difficult to theoretical model the flaming ignition of composite material due to the complex physical and chemical processes that occur during decomposition. When composite is exposed to a heat source, it can crack and delaminate. The complexity of these processes does not allow easy analytical predictions. Nevertheless ignition models proposed in this section have been found to give good estimation of the ignition delay time of some composite.

Usually, the ignition delay time t_{ig} can be defined as [Quintiere (2006)] :

$$t_{ig} = t_{ch} + t_r + t_d \tag{14}$$

where t_{ch} is the denoted time (s) needed for the flammable mixture to proceed to combustion once at the pilot; t_r is the diffusion time (s) needed for the flammable fuel concentration and oxidizer to reach the pilot; and t_d is the condition heating time (s) for the composite to achieve the decomposition temperature. Therefore, the for piloted ignition, it appears that $t_{ig} \approx t_d$ [Torero (2008)].

For high incident heat fluxes where the ignition temperature is attained very fast, thus t_{ig} is much less than the characteristic time $t_c = (k\rho C_p)/h_{ig}^2$, Carslaw & Jaeger (1959) defined analytically the ignition delay time of a thermally thick solid with the expression:

$$t_{ig} \approx \frac{\pi}{4} \frac{(k_s \rho_s C_{p,s})(T_{ig} - T_0)^2}{(\dot{q}_i'')^2} \tag{15}$$

This term reflects that the ignition delay time is independent of the total heat transfer term h_{ig} but depend on the incident heat flux $\dot{q}_i''$, the global thermophysical properties and the ignition temperature.

For low incident irradiance level, where $t_{ig} \geq t_d$, the ignition delay time is defined by:

$$t_{ig} \approx \frac{h_{ig}^2}{\pi k_s \rho_s C_{p,s}} \left[1 - \frac{(\dot{q}_i'')^2}{h_{ig}^2 (T_{ig} - T_\infty)^2} \right] \tag{16}$$

A very similar analysis can be conducted for thermally thin composite material:

$$t_{ig} \approx \frac{L \rho_s C_{p,s} (T_{ig} - T_0)}{\dot{q}_i''} \tag{17}$$

where L is the thickness. A comprehensible data review of this expression is provided by Babrauskas (2003). In this expression it is assumed that the heat losses are negligible and the subtract is an inert thermally thick and opaque solid. These equations have been proven to be accurate in the theoretical determination of the ignition delay time for thermal thick specimen such as wood and plastics but not polymer composite.

Various expressions derived from Carlaw et Jaeger, have been performed to predict the time-to-ignition [Bushman (n.d.), Abu Zaid (1988), Smith & Satija (1981), Grenier (1998), Mikkola & Wichman (1989), Shields et al. (1994), Mikkola (1992) and Babrauskas (2003)] indicate however that there is much confusion about how to present and interpret experimental data (see correlations Hallman (1971), Quintiere & Harkleroad (1985), Tewarson (1993)). It also states that the correlations derived from experimental data to determine the time-to-ignition must have a theoretical basis. In fact, the author advocates the use of correlations proposed by Abu-Zaid, Mikkola and Wichman or those proposed by Janssens (1993).

2.5.3.3 Ignition temperature and thermal effusivity

The minimum incident heat flux can be evaluated using the approach of Janssens (1993). It suggests to plot the transformed experimental ignition time ($t_{ig}^{0.55}$) versus the incident radiant heat flux $\dot{q}_i''$. This approach leads to a hyperbolic curve with the asymptote given the value of the minimum ignition energy of $\dot{q}_{min}''$. Below this value, the material does not ignite because the energy intake is too low. The minimum value of heat flux is an extrinsic property that depends on the material boundary conditions associated with heat transfer equations. Once $\dot{q}_{min}''$ is found, the ignition temperature T_{ig} can be obtained by an iterative approach in solving Eq. (9).

$$a_s \dot{q}_{min}'' = h_{cv}(T_{ig} - T_0) + \varepsilon\sigma\left(T_{ig}^4(t) - T_0^4\right) \tag{18}$$

When the thermophysical properties are not known, it is possible to estimate the thermal effusivity b ($J.K{-}1.m^{-2}.s^{-1/2}$) for a thermally thick composite material from the slope a_{slope} of the line:

$$b = \sqrt{(a_{slope}\, 0.73\, \dot{q}_{min}''\, h_{ig}^{-1.1})} \tag{19}$$

and for a thermally thin material:

$$\rho c = \frac{1.03 h_{ig}}{L\, \dot{q}_{min}'' a_{slope}} \tag{20}$$

From these observations, Tewarson (1993) introduces the thermal response parameter (TRP) concept $[kW.s^{0,5}.m^{-2}]$ which characterize the heating up of material.

$$TRP = (T_{ig} - T_0)\sqrt{b} \tag{21}$$

3. Chemical processes in gas phase

When the onset of thermal decomposition occurs, the matrix polymer of composite begins to devolatilize in very small quantities in-depth at $x = \delta_p$ on Fig. 2. Heating up the composite material leads to increase the fuel mass flux [Eq. 10]. The gas fuel encounters the ambient oxidizer close to the solid surface and if the condition is sufficient, this gas mixture can ignite. However, gas mixtures consisting of combustible, oxidizer, and inert gases are only flammable under certain conditions. Ignition of gas fuel is possible if and only if the fuel concentration are comprised between the lower flammable limit (LFL), i.e. the leanest mixture that still sustains a flame, and the upper flammability limit (UFL) which gives the richest flammable mixture.

As discussed in the previous section, this condition is not sufficient and flaming requires local contributions of energy. When the process includes an outside source (pilot flame or electric spark) the gas phase processes are strongly simplified and the influence of environmental variables are reduced. In these cases, ignition can be assumed at the moment where a LFL is attained at the local of the pilot. The process of auto-ignition is more complex and it is not practical to rely the auto-ignition to describe the susceptibility of composite material to ignite. It must be highlighted that in reality, most ignition scenarios can occur following the pilot flame process. To attain the LFL at the pilot location, it is necessary to resolve the momentum and mass transport equations simultaneously. This can be done using the surface boundary conditions explained above.

Once ignition has been achieved, a flame can propagate through the regions where a flammable mixture is present, consuming the reactants. Independent of the flow field, it is most likely that a flammable mixture is established close to the solid composite surface. Flaming combustion is a phenomenon of oxidation defined by a large number of irreversible chemical reactions in gaseous phase. The result is an exothermic reaction in the gas phase that leads to a self-sustained burning of the fuel. The exothermicity of reactions leads to a heat release resulting from the rupture of bonds between atoms of fuel and the creation of new molecules more stable chemically. This exothermic reaction can be represented by expressions similar to those in Eq 1 that could include several hundred different reaction steps in the gas phase. These reagents are disappearing to form products at a rate that depends on the concentrations of gaseous species, temperature and pressure according to very complicated mechanisms. The products of intermediate reactions are often unstable and prone to react with radicals, especially to oxidize. Under ideal conditions, the oxygen in the air combines with radical carbon and hydrogen to produce carbon monoxide and water. However, some radicals can react together to form polycyclic aromatic hydrocarbons. In flames, these compounds react with oxygen molecules so that small particles condense and agglomerate to form the *soot*.

When the flame is well established, the devolatilization rate determines the combustion condition: if a flame can continue to exist or if the combustion reaction ceases after the gas phase mixture is consumed. As discussed previously, the combustion and pyrolysis rate constitute an auto-catalytic process. The flame heat feedback enhances the devolatilization. If pyrolysis rates are not sufficient, the flame is extinguished but continuous pyrolysis leads once again to the formation of a flammable mixture and subsequent re-ignition. This manifests itself as a sequence of flashes that precede the establishment of a persistent flame over the combustible solid. This process is generally associated to "flash point" of the liquid fuels and can be used for solid fuels [Atreya (1998)]. The flow field and the supply of fuel define the characteristics of the diffusion flame established on a composite surface. The rate at which both reactants reach the flame zone defines the flame temperature and thus the characteristic chemical time. Furthermore, the burning of polymer matrix plays an important part in the fire growth and the mechanisms of fire. It determines the fuel consumption (or burning rate), the flame height and the maximum heat and smoke release. These ones influence some characteristics of fire such as the reduction of oxygen, the strapline of the flame, the solid temperature and the radiation on adjacent surfaces. The fundamental understanding of the mechanisms controlling the combustion of a combustible surface seems necessary to characterize the material as it provides reliable information on the behaviour of the solid in a real fire.

3.1 Heat released

The essential property characterizing quantitatively the intensity of fire is the heat release rate $\dot{Q}''$ or HRR ($kW.m^{-2}$). It is the rate at which the combustion reaction produces heat. It is a function of the decomposition rate of polymer matrix $\dot{m}''_p(x,t)$ ($kg.s^{-1}$). The heat release rate is dependent on material (chemical composition, fibre content and architecture) geometry, environment condition and external irradiance levels as shown by Gibson et al. (2004). The relationship of these two quantities can be expressed as:

$$\dot{Q}'' = \Delta h_c \, \dot{m}''_p \tag{22}$$

where Δh_c is the effective heat of combustion ($kJ.kg^1$). Prediction of the heat release rate is a complex phenomena that involves calculating the pyrolyzate rate [See Eq. 9] based mainly on two factors, the heat transfer into the solid and a pyrolysis kinetic mechanism.

3.2 Gaseous species released

During the thermal decomposition and combustion of material, the generation of gaseous products are issued either from the solid phase or from reactions in gas phase, as shown in 4. Gases molecules (as free radical) and some of toxic gases come from the breakdown of the chemical bond in the solid phase. For example, the stable molecules such as hydrogen chloride HCl or hydrogen bromide HBr are slightly affected by the flame when material ignites. Others gas such as aldehydes and hydrogen cyanide HCN are dependent on the time residence in the flame and can be strongly modified by the flame. The radical chain reactions in the gas phase lead to the end products of combustion, typically carbon dioxide (CO_2), sulfur dioxide (SO_2) or nitrogen oxide (NOx) etc. Species such as carbon monoxide (CO) can be generated during the devolatilization of the solid phase or produced in gas phase by oxidation reaction of hydrocarbon. Velocity of CO formation depends of the type of hydrocarbon, the temperature, the local concentration in O2 and the residences times. Velocity of the CO formation depend of the type of hydrocarbon, the temperature, the local concentration in O_2 and the residence times. A variety of other gases can be produced during the combustion of composite material [Hume (1992), Sorathia (1993), Tewarson (1993), Sastri et al. (1999), Marquis et al. (2011)].

The amount of gaseous products and the diversity of the species can be influenced by: (1) the composition of the matrix; (2) the reinforced fibre and architecture; (3) the geometry and orientation of the composite; (4) the decomposition processes (char formation, delamination, crack...); and (5) the fire conditions (oxygen content, pressure and temperature).

For a given composite, the analysis of Marquis et al. (2011) shows that the kinetics of mass loss and production of species depend on the oxygen concentration and the incident radiant heat flux on the material (or ambient temperature). The depletion of oxygen concentration leads to an increase of unburnt, namely: CH_4, C_2H_4 and $HCOH$. These ones depend on the composition of the matrix. For a given O_2 concentration, it can be seen that the mass loss rate and the gas production rate regress linearly with the irradiance level. This behaviour is the result of both of the reduction of oxygen diffusion processes in the solid phase and the thermal balance at the surface of the specimen. This strong dependence of thermal degradation and gases release in bi-variables makes it difficult to model the combustion of a composite material in the gas phase.

To understand the mechanisms operating in the gas phase, it is often necessary to accurately study the oxidation kinetics of gaseous fuels. Depending on the reaction mixture composition and temperature of the medium, there are many reaction pathways to describe the transition

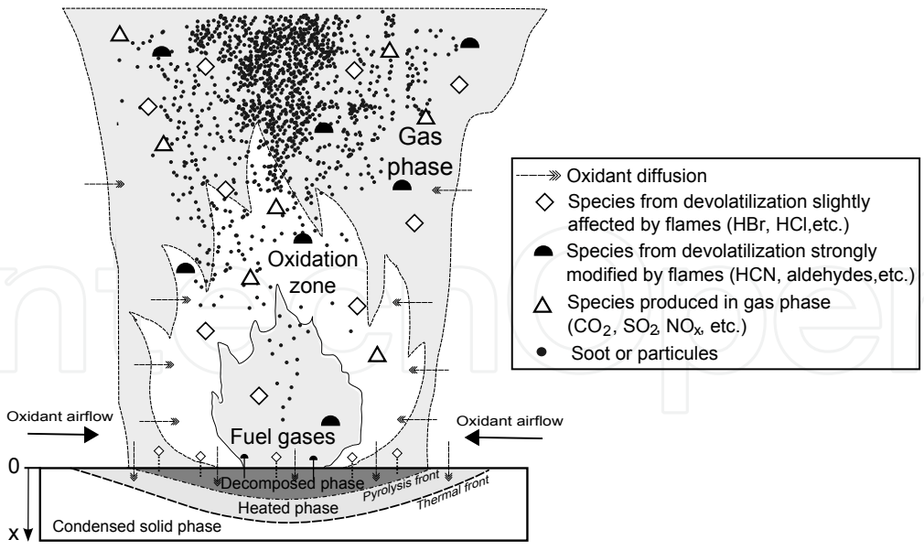

Fig. 4. Production of gaseous species from the devolatilization process of solid phase.

from a reactive to a product, usually irreversibly. This reaction mechanism may be represented at different levels of complexity, ranging from a simple overall reaction (less than 10 reactions and about 4 or 5 species) to a detailed mechanism including sometimes more than hundreds of species. Generally, these detailed mechanisms are established to model the combustion of a single gas species. Establishing a model reflecting the oxidation of gaseous fractions from a polymer material is tricky because this material produces a gas mixture rich in CO_2, CO and light hydrocarbons. In fact, the size of a detailed reaction scheme for describing the oxidation of a gas mixture representative of the gases emitted by the polymers can quickly become a serious handicap. Actually, using detailed combustion chemistry is impossible within fire simulation models. This constraint implies reducing the size of the reaction mechanism while trying to conserve its predictive potential. Because of the simplicity of the models used to represent the chemistry of combustion, it is futile to try predicting precisely the definition of chemical species of a multi-fuel sandwich composite from a global reaction [Marquis (2010a)].

4. Surface flame spread and fire growth

The previous section has given the reader a feel for the various approaches taken for pyrolysis modelling, identified some of the strengths and weaknesses and examined the fundamental transport occurring within composite material. Although microscale transport phenomena were emphasized, the ultimate goal of modelling is the prediction of large-scale fire behaviour. For this reason, the prediction of surface flame spread and fire growth are fundamental to model the fire contribution of composite material.

4.1 Surface flame spread

The rate at which a fire develops depends on how rapidly a flame can spread from point to ignition to involve an increasingly larger area of composite material. So the surface flame spread on composite material is a subject of interest on fire safety because it influences the fire growth and the heat release rate. Surface flame spread is the result of interactions between the gaseous phase and the condensed phase. It can be represented by a moving combustion

wave in the vicinity of a pyrolyzing region on the surface which acts as a fuel source: the flame front acts as an ignition pilot that initiates the ignition of pyrolyzed fuel leaving the surface. Enough heat must be transferred from the flame to the unburnt material ahead of the flame to decompose the polymer matrix and allow the surface flame spread. During the devolatilization, the gaseous species is then diffused through the decomposed phase (fibre/gas) and convected away from the surface, mixing with the oxidizer and generating a flammable mixture ahead of the flame leading edge, which is then ignited by the flame. The flame spread rate is therefore determined by the ability of the flame to transfer the necessary heat to devolatilize the polymer matrix and to ignite the fuel mixture ahead of it.

Flame spread characteristics are affected not only by the mechanism in solid decomposition (thickness, polymer composition, geometry, fibre content, etc.) but also by other factors such as flow configuration, the possible presence of an external source, environmental condition (oxygen level, temperature, pressure, gravity) and the orientation of solid composite. Flame spread over solid fuel includes two characteristic flame configurations. Either (1) *flow-aided flame spread* where the flame spread in the same direction as the oxidizing flow due to wind or buoyancy or (2) *opposed flow flame spread* which refers the flame spread in the opposite direction as the oxidizing gas flow. Furthermore, the surface flame spread process on composite material depends on mechanisms occurring both in the gas phase and the solid phase. In the gas phase, the dominant phenomena are the flow configuration, the geometry of the flame, chemical reactions and mechanisms of mass transport and heat transfer (radiation, convection and conduction) from the hot mixture of reacting gases and the combustion products above the pyrolyzed region to the unburned fuel surface. In the condensed solid phase, the flame spread is determined by the composition and geometry of composite, the heat flow on the surface, the heat diffusion unto the composite (thermal thickness) and the kinetics of pyrolysis. Progresses were made in the understanding of phenomena through theoretical sophistication and laboratory experiments. An extensive research literature exists for these class of flame spread problem, see the comprehensible reviews of [Drysdale (1998), Quintiere (2006), Fernandez-Pello (1984), Hasemi (2008) Hirano (1991) Williams (1976)].

Some noteworthy basic studies of surface flame spread allow to model surface flame spread. A great amount of theoretical and experimental work of various degrees of complexity relative to the flame spread problem has been carried out. As long as surface flame spread is discussed for the assessment of fire safety of composites materials, these phenomena are generally modelled as a thermal process. Generally these formulae are able to describe qualitatively the dependence on environmental conditions and property values of the solid fuel, when phenomena are controlled by heat transfer mechanisms. Given the strong interactions between the solid and gas phases, it is necessary to make some simplifications to the basic model. More comprehensible mathematical model includes balance equation for both gas and solid phases and need a numerical treatment.

4.2 Fire growth on composite structure

Until recently, models able to analyze the fire behaviour of composite material were not available. Thus, the conventional approach to evaluate the fire response of composite material consisted in performing fire tests at real scale on selected components of the considered whole structure. These tests can offer a lot of information about the structure integrity of a given design for specific test conditions. However, the results of such tests are usually difficult to extrapolate to other scenarios, making very costly and complex performance demonstration protocols relying only on experiments tests.

From the 2000s, several approaches of fire growth models have been developed. Despite the simplified nature of this type of fire growth modelling and its inherent uncertainties, good agreement between calculated and prediction has been demonstrated for complex material such as fire retarded composite [Lattimer et al. (2003)]. The major progress has been made towards the coupling of first principles based condensed phase fuel general models to computational fluid dynamics (CFD) that simulate the gas-phase fluids dynamics, combustion processes, and heat transfer aspects of a fire [Mc Grattan et al. (2010)]. Numerical simulation may be a powerful tool for the prediction of reaction to fire of composite material, provided that all the main chemical and physical processes are taken into account even with some simplifications. The primary advantage of this approach is the flexibility and the possibility of a rapid low-cost assessment of the fire performance compared to an analytical approach. Nevertheless, a CFD code based fire model requires an understanding of the processes occurring both in the solid phase and the gas phase. A coupled pyrolysis/CFD fire model offer the possibility to consider complex geometries and ignition scenarios, and to evaluate the impact design change. Solid phase pyrolysis models have been coupled to CFD for simulating large scale fire growth [Lautenberger (2009), Marquis et al. (2009), and (2010b)] and real scale fire [Gutierrez et al. (2008), Marquis (2010a)].

A major obstacle impeding heal world application of fire growth modelling is the difficulty associated with determining thermophysical properties and understanding thermal, chemical, physical and failure processes which control the degradation (e.g. species formation, devolatilization, chemical kinetic, structural change, evolution of thermophysical properties, fibre presence, fibre interactions, the link between in-depth decomposition and its effects on the structural behaviour). The need to understand the mechanisms in gas phase (formation and oxidation of soot, transport processes) is therefore added, to ensure a correct understanding of heat transfer into the solid phase. This strong dependence between theses two phases leads to a physical system whose analysis is not easy.

The phenomenon analysis is even more complicated because many processes are interdependent and do not occur when isolated from each other. Understanding these processes and the way they interact is essential to analyze and to predict the fire behaviour and surface flame spread. The task is more complicated for composite material, because the polymer composite used in everyday life represents such a diversity of compositions (copolymers, presence of additives ...), physical or geometrical (architecture of fibre...), that work is still needed before assuming a prediction of certain conditions of ignition and flame spread.

Due to a lack of knowledge on the subject and the complexity of the physical and chemical processes, it is necessary to have a methodology that includes successive validation steps at increasing scales. This approach allows better assessment of the final quality of numerical simulations to predict all the phenomena of fire growth on a composite material (decomposition process, ignition, combustion and surface fire spreads) whatever the geometry and the orientation is. This complex approach was successfully applied by Marquis (2010a) and (2010b), to simulate with a CFD code, fire behaviour and fire growth on thermoset-based sandwich composite structure in well ventilated fire condition. To achieve this, the author uses a combined test-simulation approach, with increasing scale and complexity. The analysis of the fire behaviour of the material was carried out from matter scale, up to an end use representative scale, through five successive scale levels. This work shows that the multi-scale methodology development seems essential to simulate the fire growth on composite structures in a reliable way. Nevertheless, the approach showed its limits

with the thermoplastic materials (Bustamante-Valencia (2009)), mainly because of the lack of capacity of the model to treat melting, bubbling and related phenomena of thermoplastic materials during their combustion.

5. Perspective

The last decade has seen a surge of modelling being applied to fire growth composite. But the robustness of the state-of-the-art of fire growth modelling is currently stalled by a poor capability to model the burning and decomposition processes of fuel solid polymer. Current fire modelling tools fail to predict properly the fire development (e.g. flame spread and fire growth) on composite material because of the complex phenomena and hypotheses used. The consequence is that currently fire modelling cannot predict the transient evaluation of the pyrolyzate rate and mainly the heat release rate in a non-trivial scenario, particularly in an under-ventilated scenario. Mains key areas in which progress is needed concern the behaviour of the condensed phase and the heat and mass transport into the composite: (1) the consideration of the oxygen diffusion on the surface, then within the material, to develop a system of devolatilization equations including the local concentration in oxygen; (2) The consideration of the movements of the condensed phase, condition needed to model the thermoplastic matrix. Furthermore, some improvements in the flame-spread model would deal with a better understanding and description of the chemical processes both in the solid and the gas phase and radiative heat transfer. Several studies are developing methodologies to overcome this limitation and the few applications available until now offer promising results but require further investigations. This topic will be one of the most important research objectives in fire engineering of the incoming decade.

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This book contains chapters on nanocomposites for engineering hard materials for high performance aircraft, rocket and automobile use, using laser pulses to form metal coatings on glass and quartz, and also tungsten carbide-cobalt nanoparticles using high voltage discharges. A major section of this book is largely devoted to chapters outlining and applying analytic methods needed for studies of nanocomposites. As such, this book will serve as good resource for such analytic methods.

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Phone: +86-21-62489820
Fax: +86-21-62489821

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