

# MODELLING OF THE DEGRADATION OF A CARBON-EPOXY COMPOSITE MATERIAL SUBMITTED TO A COUPLED THERMO-MECHANICAL LOAD

C. Mercadé<sup>1</sup>, D. Halm<sup>2</sup>, T. Rogaume<sup>3</sup>

Institut Pprime (UPR 3346 CNRS), CNRS Université de Poitiers ISAE-ENSMA, F86960 Chasseneuil-du-Poitou, France.

<sup>1</sup>[camille.mercade@ensma.fr](mailto:camille.mercade@ensma.fr)

<sup>2</sup>[damien.halm@ensma.fr](mailto:damien.halm@ensma.fr)

<sup>3</sup>[thomas.rogaume@univ-poitiers.fr](mailto:thomas.rogaume@univ-poitiers.fr)

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## Abstract

When a carbon epoxy composite material is submitted to high heat fluxes, thermal degradation phenomena occur, leading to a loss of solid material (loss of thickness due to volatilization) and to the transformation of the “virgin” material in a more fragile material, the char, whose mechanical properties are diminished [1,2]. In order to account for the phenomena occurring during thermal aggression, it was chosen to model thermal degradation, heat transfers and mechanical damages in a fully coupled way. The final aim is therefore to obtain a predictive model describing these phenomena. In this perspective, a comprehensive finite element model is developed and its different components are described in this paper.

## 1. Introduction

Nowadays, carbon fibers reinforced polymers (CFRP) are widely used in naval, aeronautical and automotive industries. They are for example utilized in the conception of type IV gaseous hydrogen vessels, whose usual pressure is seven hundreds bars, causing very high stresses in the material. Then, in order to maintain people safety, it is necessary to predict the mechanical behavior of such a tank in case of fire. Is the composite material still able to hold mechanical loads due to the pressure during and after this exposition to high heat fluxes.

In the literature, it has been shown that when exposed to fire, CFRP turn into a material whose mechanical properties are weaker than the ones of the virgin material [1]. This decrease of the mechanical properties following an exposition to fire was studied by Mouritz et al. [1]. It was highlighted that when such a composite material is submitted to high heat fluxes, thermal degradation phenomena occur, leading to the formation of a carbonaceous material named “char”. Feih et al. [2] have set up a predictive model, allowing the determination of the time to failure of composite coupons submitted simultaneously to high heat fluxes and to a compressive load. It is found that the time to failure is decreasing while heat flux is increasing. Thus, the influence of char on the coupons early failure was proved. Beyond this demonstration, predicting a structure behavior for every thermal and mechanical load, at product scale, seems necessary. This aim might be reached thanks to multiphysics coupled simulations.

Thus, some recent works have studied hydrogen tanks and their fire behavior, namely [3] and [4], coupling thermal degradation, heat transfers and mechanical behavior. Nevertheless, those studies have some limitations:

- When mechanical damage appears, it is often represented by an ultimate stress criterion [2].

- The mechanical damage is hardly represented by thermodynamic internal variables; in general only in-plane damage phenomena are considered (no delamination [3], which is a frequent cause of failure);
- In some studies [4], there is no comparison between results of modelling and experimental data.

In this context, this paper introduces a methodology coupling the main mechanisms met during the exposure of a high pressure vessel to a fire, so as to predict the CFRP structure behavior. The implementation of this model is synthetized in the following and results are presented at coupon scale. The final aim is the prediction the CFRP structure behavior not only at the coupon but also at the product scale, as well on the mechanical level than on the heat transfer level and the thermal decomposition.

## 2. Multiphysics couplings

The description of the physical problem leads to the distinction of three different coupled domains: thermal degradation, heat transfer and mechanical damage.

The simulation of each mechanism is extensively dealt with in the literature: damage models are capable of determining the mechanical degradation of composite structures subjected to any loading [5], thermal degradation models simulate the transformation of composite into char [6] and the solving of the heat equation provides the temperature fields [6]. However, when a composite structure is simultaneously subjected to a mechanical load and a fire exposure, strong interactions exist between these different mechanisms. For example:

- Influence of temperature on thermal degradation: the material chemical decomposition and the kinetics of char formation depend on temperature (*via* an Arrhenius law) (cf section 3.1).
- Influence of thermal degradation on temperature: thermal parameters depend on thermal degradation. Indeed, char has diminished thermal properties compared to virgin material [1,2]. Yet, this coupling is only implicitly introduced in this paper, with a temperature dependence of thermal capacity [6].
- Influence of temperature on mechanical behavior: the mechanical properties obviously depend on temperature, for instance strength and stiffness. Indeed, when the resin undergoes its glass transition, the stiffness in the direction perpendicular to the fibers changes [7]. Thus, this elastic modulus depends on the temperature. Besides, due to the resin thermal expansion, internal stresses are generated by temperature [3]. Additionnally, mechanical damage at ambient temperature has to be considered.
- Influence of mechanical behavior on temperature: thermal properties depend on the mechanical damages. For instance, when delamination occurs, the conductivity in the direction normal to the ply separation is reduced. Nevertheless, this coupling is assumed to be neglectible. Indeed, this coupling is already considered when conductivity of char is reduced following thermal degradation, which was the main cause of delamination.
- Influence of thermal degradation on mechanical behavior: it is one of the most important couplings. Indeed, thermal degradation makes the material more porous and brittle as the material decomposes, losing thickness and strength [1-2].
- Influence of mechanical behavior on thermal degradation: some studies [8] have shown a certain influence of mechanical stresses on thermal degradation, but this influence is found to be weak in this paper so it is neglected here.

## 3. Detailed models and equations

In this section are briefly introduced the three models necessary to the global modelling, namely thermal degradation model, mechanical model and heat transfer model.

### 3.1. Thermal degradation model

Beyond a given temperature, thermal degradation of the resin occurs. In spite of the complexity of this phenomenon, involving hundreds of chemical reactions [9], it is usually modelled using several modified Arrhenius laws, for instance in [10]. Yet, in the present study as in many other studies dealing with thermomechanical modelling of composite materials [2,3,4], thermal degradation and the consecutive mass loss is approached using only one reaction, modelled by an unique modified Arrhenius law which can be expressed with eq. 1, 2 and 3. Eq. 1 introduces  $\alpha$  the thermal degradation variable, also called conversion ratio, a function of  $m_0$  the initial mass of representative elementary volume,  $m$  its mass at time  $t$  and  $m_f$  its mass at the end of the reaction. Eq. 2 expresses the relationship between the mass loss rate  $\frac{dm}{dt}$  and the kinetic rate of the reaction of thermal decomposition expressed in eq. 3, where  $v$  is the stoichiometric factor. Finally, Eq. 3 gives the expression the reaction rate  $\frac{d\omega}{dt}$  based on a modified Arrhenius law, with  $A$  the pre-exponential factor,  $E$  the activation energy,  $T$  the temperature,  $R$  the gas constant, and  $n$  the reaction order.

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (1)$$

$$\frac{dm}{dt} = \frac{v * d\omega}{dt} \quad (2)$$

$$\frac{d\omega}{dt} = A * m^n * \exp\left(-\frac{E}{RT}\right) \quad (3)$$

The kinetic parameters  $A$ ,  $E$ ,  $n$  and  $v$  are unknown and then determined from Thermo Gravimetric Analyses (TGA) using inverse optimization methods, for instance genetic algorithms [11]. The reaction considered here is the transformation of composite into char (Eq. 4) :



The kinetic parameters considered in the present work have been determined from TGA experiments using a genetic algorithms method and are the following (Table 1):

**Table 1.** Kinetic parameters

$A$	$n$	$v$	$E$
(-)	(-)	(-)	(J/mol)
15 849	0.8	0.83	199 000

### 3.2. Mechanical behavior

Prior to any mechanical or thermal material degradation, each composite ply has an orthotropic behavior. Each stiffness component is temperature-dependent. This dependence is particularly marked around the glass transition [7].

The five different types of degradation modelled here are fiber breakage, fiber-matrix debonding, delamination, matrix cracking and thermal degradation or conversion ratio called  $\alpha$  in the previous section. It is a very special damage, being the only chemically caused damage taken into account *via* a mechanical formulation, as explained later on. These five damages can be classified into two

categories: the brittle ones and the progressive ones. Fiber breakage, interface debonding and delamination are brutal mechanical damages with a Hashin strain-based formulation [12]. More precisely, beyond a threshold (different for each type of damage) expressed in term of critical strain, damage initiates. Depending on the mechanical behavior type (brittle or soft), damage internal variables grows at a different rate. Thus, in the case of a brittle mechanical behavior, damage internal variable grows rapidly with strain, until its maximum value is attained. The damage variable  $d$  begins to evolve when the criterion  $d_{ini\_crit} = 0$  is reached. The general expression of this damage initiation criterion  $d_{ini\_crit}$  is the following (Eq. 5):+

$$d_{ini\_crit} = \delta_{eq} - \frac{(\delta_{eq}^f * \delta_{eq}^0)}{\delta_{eq}^f + d * (\delta_{eq}^0 - \delta_{eq}^f)} \quad (5)$$

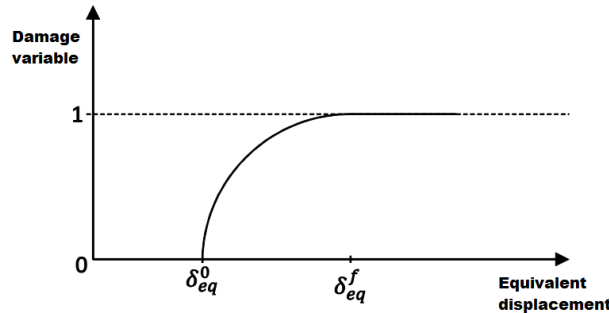
Where:

- $d$  is the damage variable influencing elastic moduli. It is calculated thanks to the expression of the initiation criterion when this one is equal to zero.
- $\delta_{eq}$  is the equivalent displacement variable and can be expressed as a function of strain. Its expression is given for instance for fiber damage:

$$\delta_{eq}^{fiber} = L_c * \sqrt{\varepsilon_{11}^2 + \beta * \varepsilon_{12}^2} \quad (6)$$

where  $L_c$  is a characteristic length,  $\varepsilon_{11}$  is the strain in the direction of fibers and  $d\varepsilon_{11}$  its increment,  $\beta$  is the relative weight of in-plane shear relatively to the traction of fibers, and  $\varepsilon_{12}$  is the in-plane shear strain.

- $\delta_{eq}^0$  is the equivalent displacement when damage initiates.
- $\delta_{eq}^f$  is the equivalent displacement when damage has reached its maximal value, as the following diagram illustrates it:



**Figure 1:** Damage variable evolution

In addition, the material is affected in a different way by each brittle damage variable: fiber damage affects the elastic modulus in the direction of fibers, while fiber-matrix debonding affects the elastic modulus in the direction perpendicular to fibers. Both variables affect the in-plane shear modulus. Delamination variable affects the out-of-plane elastic and shear moduli.

In opposition to the previously mentioned damages, matrix cracking and thermal degradation variables are progressive. Matrix cracking only affects the in-plane shear modulus and thermal degradation variable affects every direction except the direction of fibers. The evolution law of the thermal degradation variable is expressed in section 3.1. The evolution law of damage variable for the matrix cracking  $ds_{12}$  is the following (Eq. 7):

$$ds_{12} = SAT * \left( 1 - \exp \left[ - \left( \frac{\varepsilon_{12} - \sqrt{F_I^{\rho S}}}{C_I^y} \right)^n \right] \right) + C_2^y * (\varepsilon_{12} - \sqrt{F_I^{\rho S}}) \quad (7)$$

The parameters  $SAT$ ,  $\sqrt{F_I^{\rho S}}$ ,  $C_I^y$ ,  $C_2^y$  et  $n$  are identified by the mean of experimental results, depending on the wanted evolution law:  $\sqrt{F_I^{\rho S}}$  defines the initiation damage strain,  $C_I^y$ ,  $C_2^y$  et  $n$  are rate constants controlling the damage evolution (rate and form),  $SAT$  enables to set the damage variable at another value than 1.

Knowing every damage variable named  $d$ , elastic modulus and Poisson's ratio, it is necessary to compute every member of the elasticity damaged tensor  $C(d)$ , in which elastic moduli are affected in the way explained above by mechanical and thermal degradation damages. Its expression can be summed up by Eq. 8 :

$$C_{ij}(d) = E_{ij} * \prod_{k=1}^n (1 - d_k) \quad (8)$$

where  $C_{ij}$  is the  $ij$ -th term of the stiffness tensor,  $E_{ij}$  is the corresponding term of the elasticity tensor,  $d_k$  is one the damage affecting this term.  $d_k$  may be a mechanical damage or a thermal degradation damage. It is highlighted that in this model, thermal degradation is acting in the same way as mechanical damage. Once the elasticity damage matrix calculated, the stress tensor is obtain with Eq. 9

$$\sigma_{ij} = \varepsilon_{ij} * C_{ij}(d) \quad (9)$$

### 3.3. Heat transfers

As mentioned previously, the thermal degradation variable has to be calculated accurately, like all the other degradation variables. Hence, the temperature has to be determined with a quite high precision too. Thus, to solve the heat transfer equation (Eq. 10) in every point of the material, conduction and production of heat by the thermal degradation are considered.

$$\rho C_p(T) \frac{dT}{dt} = -div\{\lambda * [-grad T]\} + \rho \Delta H^r(T) \frac{d\alpha}{dt} \quad (10)$$

where  $\rho$  is the density,  $\alpha$  the thermal degradation variable,  $\Delta H^r(T)$  the enthalpy of pyrolysis,  $T$  the temperature,  $C_p$  the thermal capacity and  $\lambda$  the conductivity.  $C_p$  depends on temperature, whereas  $\lambda$  and  $\rho$  are constants [6]. The left hand term is the absorbed flux. The first term in the right hand side accounts for heat conduction and the second term for the heat produced by thermal degradation.

According to the heat equation, this step requires the calculation of  $\rho \Delta H^r(T) \frac{d\alpha}{dt}$ , where  $\frac{d\alpha}{dt}$ , the thermal degradation rate, is known, and  $\Delta H^r(T)$ , the enthalpy of pyrolysis, has to be calculated, which is done as follows (Eq. 11):

$$\Delta_r H(T) = \Delta_r H(T^0) + \int_{T^0}^T \Delta_r C_p^0 dT \quad (11)$$

where  $\Delta_r C_p^0$  is the known thermal capacity at temperature T and constant pressure.  $T^0$  Is the reference temperature and  $\Delta_r H(T^0)$  is the known enthalpy reaction at reference temperature.

#### 4. Numerical implementation

In this section, the numerical implementation of the couplings described in section 2 is detailed, considering models chosen in section 3, in a FEA context. The mechanical and thermal loadings are applied in an incremental way. Each increment comprises several steps, detailed here. The calculation of stress tensor  $\sigma$  requires the update of the state and internal variables (mechanical strain  $\epsilon$ , mechanical damages d, thermal degradation variable  $\alpha$  and temperature T). Each variable is known from the previous increment.

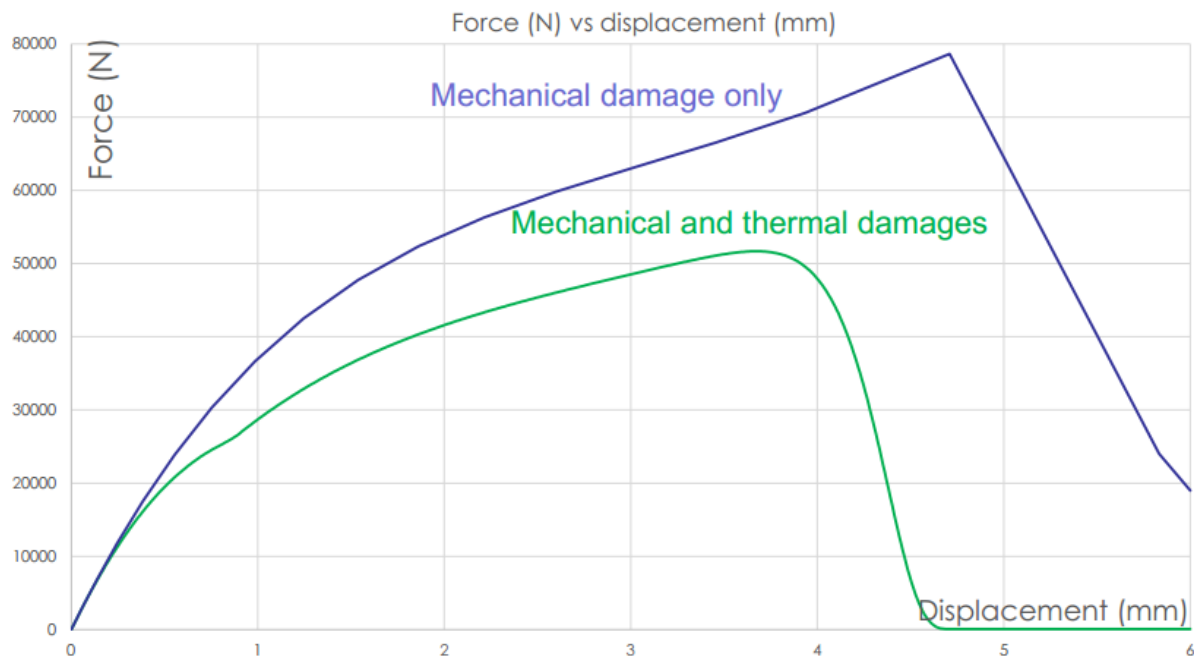
First, from the temperature of the previous increment, the thermal degradation variable  $\alpha$  is calculated, using the model explained in section 3.1. Then, it is necessary to update temperature T by solving the heat equation, given by Eq. 11. After this step, the updated temperature is known.

Regarding the mechanical behavior, the internal variables and the stress are updated in the following way:

- (i) the strain tensor increment  $d\epsilon$  is directly imposed by the FE solver, and allows one to update  $\epsilon$
- (ii) from the updated temperature, the temperature dependent mechanical parameters are calculated namely elastic moduli and failure strains.
- (iii) with the updated strains and using the mechanical model explained in section 3.2, initiation criteria are checked. If the evolution condition is satisfied, the damage variables are determined from Eq.3 and Eq.7 and the stiffness and the stress updated.

#### 5. Results

In this section is briefly presented an example of a calculation led on a carbon-epoxy composite coupon of dimensions 100mmx100mm made of 42 plies with the [45/-45] stacking sequence. In the coupled simulation the coupon is submitted to a heating rate of approximately 20 K/min and its displacement is 0.24mm/min during 1500s, whereas in the purely mechanical case, this coupon is only put under a monotonous tension at a 0.24mm/min displacement rate. In order to compare the results, the obtained force displacement curves are plotted on the same following diagram (Fig. 2):



**Figure 2:** Comparison between coupled and purely mechanical approach

As expected, the thermal degradation variable acts as a progressive damage variable: the force increase is lower in the case the coupon is heated because of the corresponding degradation. Note also the maximum displacement is lower.

## 6. Conclusion and future works

In this paper, a model coupling thermal degradation, mechanical behavior and heat transfers occurring in a CFRP material submitted to high heat fluxes is explained. The numerical implementation and some results are presented. Thermal degradation is modelled using a single reaction Arrhenius law, while mechanical behavior uses Hashin-like strain-based criteria, delamination and progressive damage, considering thermal degradation as a supplementary mechanical damage. Finally, heat transfers consider conduction, radiation and production of heat caused by the resin pyrolysis. Then, the model is implemented in a commercial Finite Element software using user subroutines, enabling a fully coupling of all phenomena in a single increment of time. First results show the important weight of temperature on the resulting displacement-force diagrams. It is noticed that thermal degradation plays the role of a progressive damage variable. Future works will allow to conclude on the respective weights of temperature, mechanical damages and thermal degradation in the loss of mechanical properties of the composite material, and also on the necessity of the full coupling methodology in order to obtain sufficiently accurate results.

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