

# COUPLED MECHANICAL–CHEMICAL SIMULATION OF AN OXIDIZED CFRP COMPOSITE

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## ABSTRACT

The aim of the present study is to better understand the scenario of the damage initiation in carbon/epoxy composites exposed to thermo-oxidative environments. To that goal, a preliminary state of the art is realized, so as to understand the mechanisms involved, in the fields of mechanics, diffusion and chemical reactions. Then, as far as some previous studies have shown that these contributions occur simultaneously and interact (as mechanics and chemical reactions, chemical reactions and oxygen diffusion..), an extensive characterization of the couplings is performed. In a second part, a numerical simulation is presented, based on a new finite element specifically developed, including all the mechanisms and couplings evidenced previously. An application is done for a composite sample, in order to evaluate the stress field inside the matrix after 200h of oxidation at 150°C under atmospheric air. Numerical predictions and experimental observations are finally compared and discussed.

## INTRODUCTION

In the field of aeronautic structures, it is now assessed that oxidation at high temperature accelerates damage kinetics of carbon/epoxy composite materials. In previous works, the influence of oxidation on damage initiation has been studied, both under thermal cycling and isothermal ageing conditions. It was shown that, in both cases, the presence of an oxidative environment accelerates the onset and accumulation of damages, mainly constituted of matrix shrinkage, fiber/matrix debonding, and matrix cracking (Figure 1).

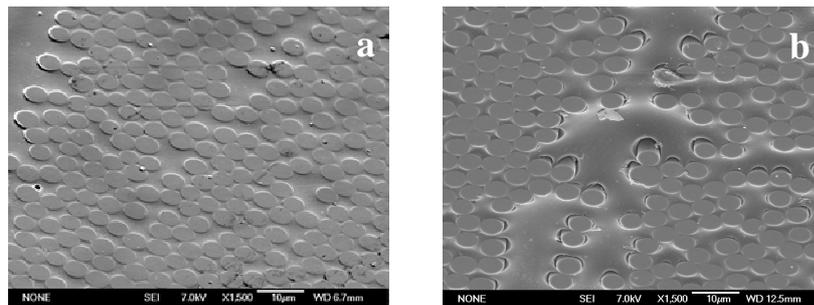


Figure 1: SEM pictures of the edges of carbon epoxy (IM7/977-2) specimen aged under vacuum (a) and atmospheric air (b).

Experimental characterizations of the oxidized material were made thanks to microscopic observations (optical microscope, Scanning Electronic Microscope, X Rays) and mechanical properties measurements (Dynamic Mechanical Analysis and Resonance method, instrumented Ultra-Micro Indentation). Moreover, the use of a specific octagonal composite laminate sample showed that, during thermal cycling in an oxidative atmosphere, the local stress field influences significantly the kinetics of

development of the induced matrix cracking [1]. On another hand, a specific mechanistic scheme has been developed by Verdu and Colin [2], validated on the 977-2 resin, and able to predict the local oxidation state inside the polymer through any oxidation test.

The study presented here is part of a research program named 'COMEDI', that was initiated at LMPM-ENSMA in collaboration with EADS-IW, LIM ENSAM-Paris and which is supported by the French Research National Agency (ANR). It concerns the durability of aeronautical CFRP composite laminates subjected to long-term ageing and especially aims to better understand the magnitude of intricate interactions which can appear between local mechanical stresses and thermo-oxidative kinetics.

In a first part, the IM7/977-2 composite material is presented. Then, an extensive characterization of the couplings is realized, in order to build a coupled model able to describe the local oxidation of the composite. The main feature of this investigation is to be as deterministic as possible, so as to limit the contribution of phenomenological relations that could narrow its application field in the future. In the end, a specific new finite element will be presented, including all the mechanisms and correlations presented in the first part, and used to present the first results capable to predict the damage onset induced by oxidation in a composite sample.

## MATERIAL

The material under consideration is a carbon-epoxy composite used in aeronautic structures, supplied by EADS IW (European Aeronautic Defence and Space Company Innovation Works, Suresnes, Fr). Its matrix is an epoxy-amine (ref 977-2) obtained by mixing two aromatic epoxy pre-polymers (DGEBF/ TGPAP) crosslinked with an aromatic diamine (DDS). The 977-2 polymer contains a thermoplastic polyester sulphone (about 30% in weight) for increasing its impact resistance. Plates of neat epoxy resin were elaborated according to a specific polymerization cycle optimized to obtain a very stable material without any effect of overheating or evolution of properties. This cycle is constituted by a 3 hours long gelation step at 150°C, a 2 hours long curing at 180°C, followed by a post-curing at 210°C under vacuum, 1.5 hours long, to obtain a supplementary cross-linking.

Many studies can be found in the literature concerning the characterization of the mechanical behavior of this composite in presence of thermo-oxidation (e.g. ref. [1, 3-6]), and the description of the chemical reactions involved in the oxidation process, leading to a specific closed-loop mechanistic scheme validated in many configurations of temperature (e.g. ref. [2, 7], recalled in Figure 2).

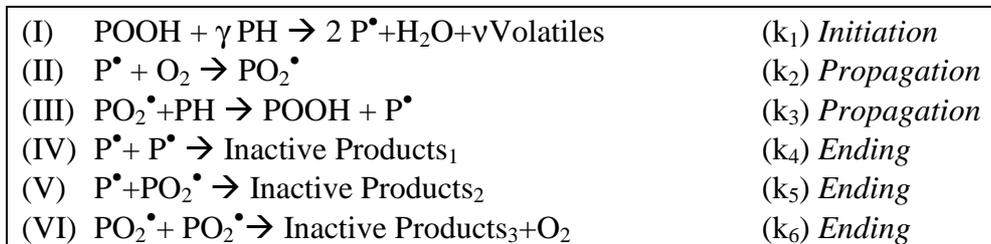


Figure 2: Mechanistic scheme developed by Verdu and Colin [2].  $\bullet$  characterizes the radicals (e.g.  $\text{P}^\bullet$ ,  $\text{PO}_2^\bullet$ ) and P stands for the polymer macromolecular chain. PH stands for an oxidizable site.

In previous studies, correlations have been investigated between this mechanistic scheme and mechanical properties (e.g. [3]), but - to the authors knowledge - no global model has been proposed, able to simulate the stress state due to oxidation inside the composite from this mechanistic model. This will be the point of the next sections. First of all, it is important to better characterize the interactions between mechanics, oxygen diffusion and chemical reactions.

### IDENTIFICATION OF DIFFUSO-CHEMO-MECHANICAL COUPLINGS

A schematic presentation of the couplings to study is presented in Figure 3:

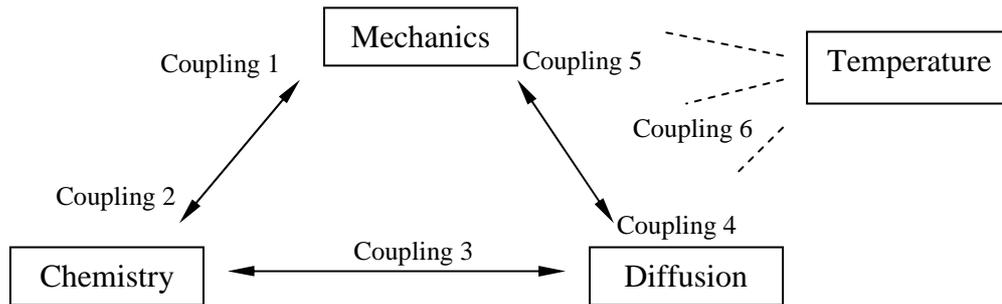


Figure 3: Schematic presentation of the couplings involved in the oxidative process.

In spite of the fact that many different chemical species are involved in the mechanistic scheme (Figure 2), the only one that will be considered as mobile -and subject to diffusion- will be the oxygen. Indeed, volatile molecules are generated by the chemical reaction (I), but these molecules are assumed to escape instantaneously from the material and supposed to be chemically neutral towards the epoxy polymer [8].

Let us analyze point by point every coupling:

Coupling 1: Concerning the influence of the physico-chemical state on mechanical behavior, a phenomenological correlation between the elastic modulus and the concentration in oxidation products -calculated from the mechanistic scheme- has been previously presented in [3], and recalled in Figure 4.

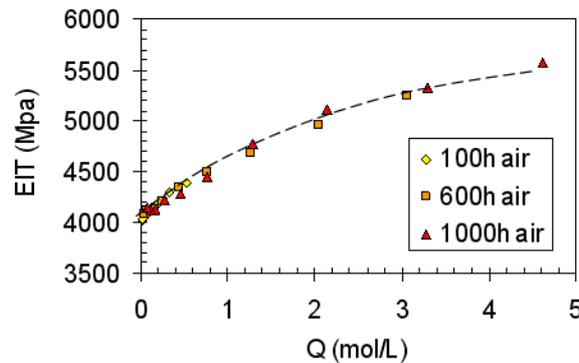


Figure 4: Correlation between the elastic indentation modulus (EIT) and the concentration in oxidation products (Q) from the mechanistic scheme [3]. Data obtained at room temperature by ultra-micro indentation after aging at 150°C for 100h, 600h, 1000h under atmospheric air.

Moreover, the shrinkage deformation due to oxidation can be obtained, as proposed in [7], from the relative mass loss and density change:

$$\overline{\varepsilon}_{shrinkage} = \frac{1}{3} \frac{\Delta V}{V} \overline{I} = \frac{1}{3} \left( \frac{\Delta m}{m_0} - \frac{\Delta \rho}{\rho_0} \right) \overline{I} \quad (1)$$

where  $m_0$  and  $\rho_0$  stand for respectively the initial mass and the initial density of the resin sample, and  $\overline{I}$  the identity tensor. Relative variations of mass and density can be calculated directly from the mechanistic scheme.

In the case of an elastic behavior for example, couplings can be directly integrated inside the following equation of state:

$$\overline{\sigma} = \overline{\overline{L}}(Q) * \left( \overline{\varepsilon} - \overline{\varepsilon}_{shrinkage} \right) \quad (2)$$

where  $\overline{\overline{L}}$  represents the fourth order stiffness tensor and  $\overline{\varepsilon}$  the second order total strain tensor.

Coupling 2: In the literature, some studies can be found concerning the influence of the stress field on reaction rates (e.g. [9]). In the light of their conclusions, it comes that no obvious correlation has been found between these two phenomena. Consequently, this coupling is neglected here.

Coupling 3: The state coupling between chemical reaction and diffusion comes directly from the local equation of diffusion, describing the evolution of the oxygen concentration with time [3, 8]:

$$\frac{d [O_2]}{dt} = \underbrace{div \Phi}_{Fickian\ diffusion} - \underbrace{k_2 [O_2] [P^\bullet] + k_6 [PO_2^\bullet]^2}_{Chemistry} \quad (3)$$

where  $\Phi$  is the mass flux of the oxygen, and  $k_i$  stands for the reaction constant rate of the  $i^{th}$  reaction from the mechanistic scheme. The diffusion is supposed to be Fickian, and the contribution of the chemical reactions comes directly from the mechanistic scheme.

Coupling 4: The influence of the local load state on diffusion kinetics is specifically investigated in this study, looking for the theoretical expression of the coupling, and then by trying to identify it experimentally. The expected formulation of the coupling was built from thermodynamics (as demonstrated in [8]) such as:

$$\frac{d [O_2]}{dt} = \underbrace{Fickian\ diffusion + Chemistry}_{eq.3} + \beta_{O_2} div \left( grad\ tr \left( \overline{\varepsilon} - \overline{\varepsilon}_{shrinkage} \right) \right) \quad (4)$$

where Fickian diffusion and chemistry contributions come directly from eq.3, and  $\beta$  stands for a coupling parameter to be determined experimentally. This means that the coupling effect should be due to a local variation of the volume deformation ( $\frac{\Delta V}{V} = tr \overline{\varepsilon}$ ), the gradient of which could generate a mass flux of the mobile specie.

In order to evidence such a coupling, specific tests are performed thanks to a dedicated device (presented in [8]), on a notched resin sample submitted to constant elongation during 48h, at 150°C in 5 bars of pure oxygen. The geometry of the sample is presented in Figure 5:

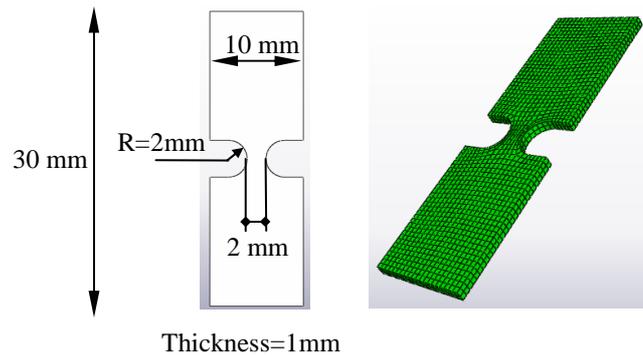


Figure 5: Working sections sketch and mesh of the notched resin sample used for the identification of the coupling between mechanics and diffusion. Each dimension is in millimeter.

The elongation to impose was chosen so as to correspond to a load at 70% of failure. A finite element simulation of the sample shows that the local stress and strain fields are clearly inhomogeneous, which is supposed to enhance the influence of the corresponding coupling term in eq. 4, as shown in Figure 6:

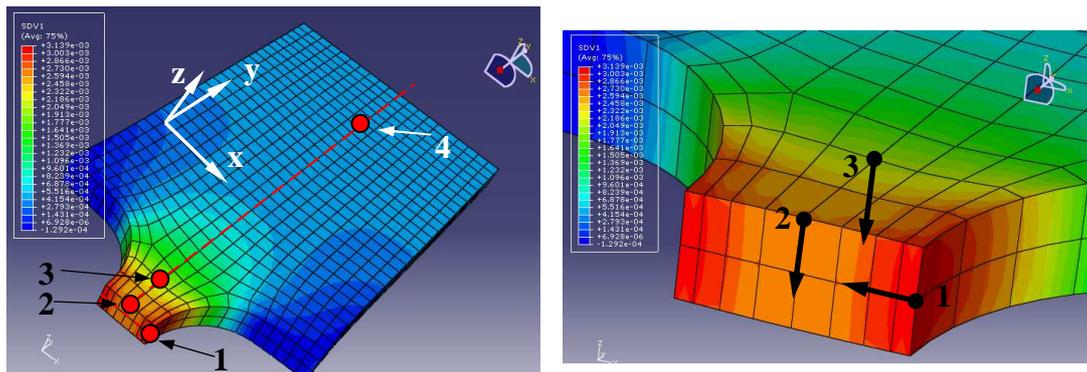


Figure 6: Volume strain field inside the notched specimen, calculated for a longitudinal applied load of 84N with elastic behavior and no oxidation. Dashed lines represent symmetry axes and circles stand for localization of ultra-micro indentation modulus profiles presented in Figure 7 (direction of profiles indicated by black arrows).

At the end of the test, the oxidized sample was then prepared and instrumented ultra-micro indentation tests have been carried out, in different locations in the specimen, as described in Figure 6 (colored circles from 1 to 4 and arrows). These particular locations have been chosen so as to characterize the oxidation in different configurations, close to the notch for a triaxial inhomogeneous deformation state (points 1 to 3) and far from it in the uniform section for an homogeneous one (point 4). From these ultra-micro indentation tests, local values of the elastic modulus of the resin can be obtained and its evolution against the distance from the edges of the specimen is shown in Figure 7, according to the location of the measure lines.

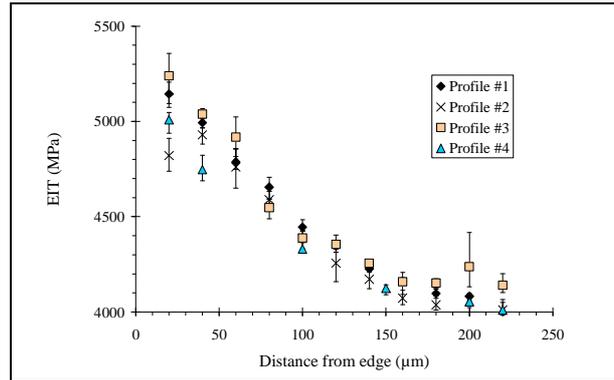


Figure 7: Elastic modulus profiles obtained by ultra-micro indentation on the notched resin sample oxidized at 150°C, 5bO<sub>2</sub>, 48h under constant deformation. Profiles correspond to the points 1-4 in Figure 6.

According to Figure 7, and considering that the intrinsic experimental scattering of the elastic modulus is around 400 MPa, it comes out that no clear influence can be attributed to the inhomogeneous deformation state present during oxidation, which means that in that case, the  $\beta$  coupling parameter of eq. 4 can be neglected.

*Coupling 5:* The diffusion has been willfully considered to be uncoupled with the mechanical behavior of the polymer since the oxygen flux is not supposed to interact with the polymer in another way than by oxidation reactions described in the mechanistic scheme.

*Coupling 6:* As far as the tests are done under constant homogeneous temperature (150°C) and considering that the heat flow generated by chemical reactions (heat of reaction) is low, the thermal coupling can be neglected, i.e. no local thermal evolution is taken into account. However, each parameter of the model has been taken as a function of temperature in the form of Arrhenius law (Energy of activation and pre-exponential factors can be found in literature [2, 7]). That dependency allows to extrapolate the model to any temperature in the range where the processes are globally isotherm. Anyhow, temperature will not be a degree of freedom in the finite element model presented in the next section.

## NUMERICAL SIMULATION

### 1.1 Description of the finite element model

A dedicated finite element has been elaborated so as to simulate numerically an oxidation test, and to calculate the stress field induced inside a composite sample.

This element is hexahedral, quadratic in displacement and concentration, and does contain 27 integration points. Its degrees of freedom are three displacements and the oxygen concentration, i.e. 80 d.o.f. by element. The concentration values of other chemical species that appear in the oxidation scheme are calculated and collected inside the state dependent variables (SVARS) since their diffusion is neglected.

The model has been implemented in ABAQUS using the “user element” UEL subroutine. The global scheme of resolution can be described as follows:

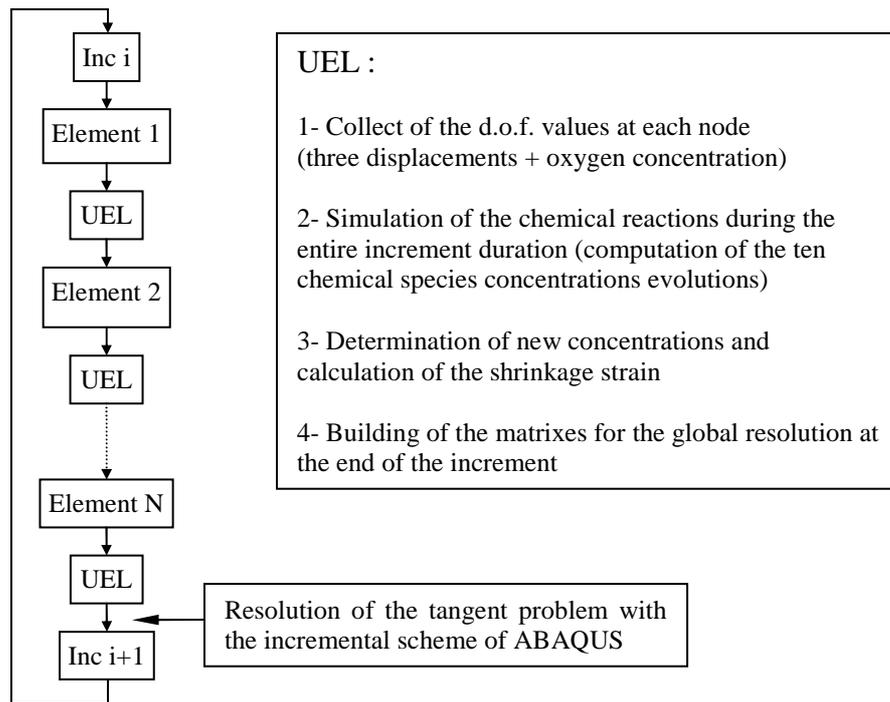


Figure 8: Schematic presentation of the algorithm of resolution of the thermo-oxidative problem on a finite element model.

According to Figure 8, an obvious problem of fluctuations arises from the fact that diffusion and reaction equations are treated sequentially in this transitory problem: while oxidation reactions are computed on each element separately, the global diffusion equations are solved at the end of the increment on the whole structure. Obviously, in some cases, oscillations can occur, as shown in Figure 9:

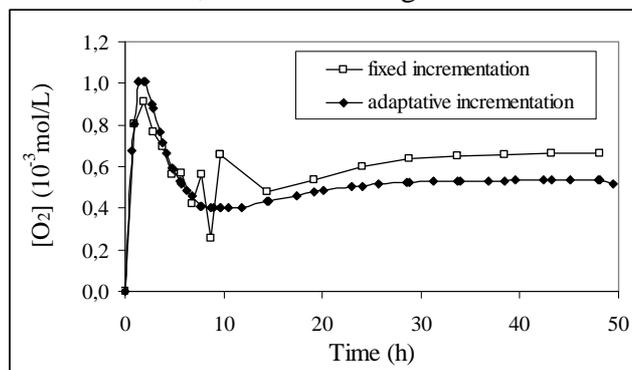


Figure 9: Fluctuations observed on oxygen concentration evolution, due to the separated resolution of chemical and diffusion problems. Local simulation of the oxidation in a resin sample at 150°C, atmospheric air, 48h.

However, an adaptive managing of increments duration has been set up, which allows to avoid this problem (Figure 9), and to get a good stability of the computation .

## 1.2 Application to a composite sample

In this section, a numerical simulation is done on a composite sample, and compared to SEM observations. The experimental test has been performed at 150°C under

atmospheric air on a unidirectional IM7/977-2 composite (Figure 10 a). First fiber/matrix debondings can be observed locally, without being generalized to the entire set of fibers (they occur preferentially close to matrix rich areas). Anyway, it can be seen in the Figure 10(a) that the damage state is already problematic, since several debondings have propagated in the low part, which represents a preferential site for further matrix cracking and deeper oxygen penetration into the polymer. In comparison, a simulation is done for 150°C, 48h under atmospheric air on the same “structure” (dimensions have been taken so as to fit at best with the SEM micrograph) (Figure 10 b). The fiber diameter is around 4 $\mu\text{m}$ , and the depth of the specimen model has been taken equal to 200 $\mu\text{m}$ , longer than the oxidized layer thickness. The mesh has been divided in two parts, one close to the free edge (50 $\mu\text{m}$  thick), much refined in order to describe at best the stress and strain gradient fields, and the other in the back (150 $\mu\text{m}$  thick), less refined because mechanical fields are there quasi homogeneous. Fibers have been considered as mechanically embedded, and symmetry conditions have been applied on all edges for all d.o.f. (except for the free edge obviously). Introduction of the oxygen in the polymer has been done directly by setting the concentration constant on the free edge, equal to 0.0033 mol/L.

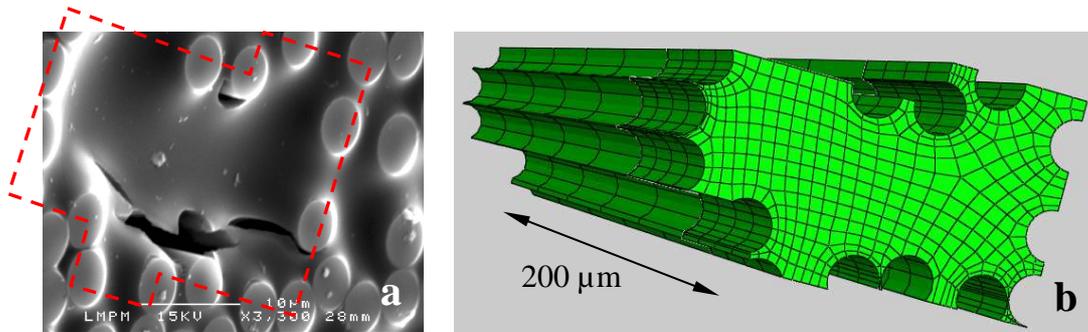


Figure 10: a/ SEM micrograph of the free edge of an oxidized IM7/977-2 composite. The dashed profile stands for the delimitation of the finite element simulation. b/ Finite element mesh that is used for the simulation.

Note: A simple viscoelastic behavior of the resin has been considered for the simulation, identified on basic experimental tests, so as to reproduce the relaxation effect while matrix shrinkage occurs.

The calculated Von Misès stress field is presented in Figure 11:

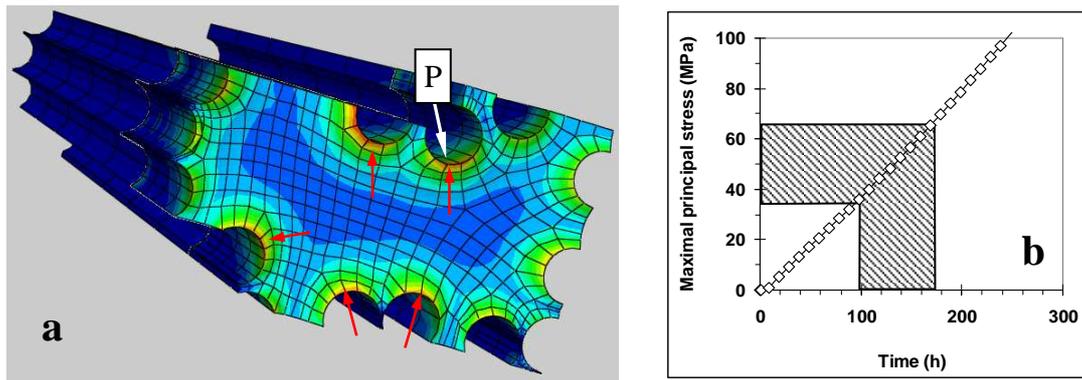


Figure 11: a/ Von Misès stress field after a simulation of 200h at 150°C under atmospheric air. Maximal VM stress is 75 MPa at point P. Red arrows show the five highest stressed interfaces. b/ Evolution of the maximal principal stress at Point P during the oxidation simulation. Grey area stands for the stress range of failure of the resin, from tensile tests in the range of displacement speed [0.1 mm/min, 500mm/min] at 150°C.

The Von Misès stress field from Figure 11(a) is in agreement with the location of damage in the composite sample, since the five highest stressed interfaces (red arrows in Figure 11) correspond to the fiber/matrix debonding locations in Figure 10.

In order to estimate the time of the first damage onset, a failure criterion is needed. As a first approximation, tensile tests have been done at 150°C on neat resin samples, for various strain rates (from 0.1 mm/min to 500 mm/min). The failure stress values have been found in the range [35-65 MPa] and using a maximal principal stress criterion, shown as a grey area in Figure 11(b). Consequently, the first damages should be expected between 100 and 180 hours approximately (see Figure 11(b)). However, this result must be considered very carefully, since it is based on the assumption that the interphase can be neglected in the debonding process (direct contact between fiber and matrix), and that failure properties are not modified by oxidation. Both hypothesis can be easily criticized, obviously, and better failure conditions are under study right now. Anyway, this simple approach of the fiber-matrix debonding is sufficient to highlight the capacities of our model.

## CONCLUSIONS AND PERSPECTIVES

In this paper, a specific model has been presented, taking into account most of the mechanisms involved during oxidation test of an epoxy resin. It has been created so as to be as deterministic as possible, in order to be extrapolated easily to any other configuration based on the same mechanisms. As far as it was observed experimentally that interactions between mechanics and oxidation phenomenon did play an important role in damage initiation and propagation, an extensive characterization of these couplings has been realized, and integrated into the present model. In particular, the coupling between diffusion and mechanics has been specifically tested and found to be neglectable in this case.

Then, a specific new finite element has been created to do 3D local computation in the vicinity of carbon fibers. It was used for modeling a real composite sample, oxidized under atmospheric air at 150°C. The obtained stress field has been studied and it was

found that the locations of the maximal stresses correspond to those of the fiber/matrix debonding observed on the free edge of the composite. As a first approximation, a simple failure criterion has been used in order to predict the time of first damages onset.

In order to make the model more accurate, works are in progress:

- first of all, the values of the shrinkage strains obtained by the model are going to be compared to experimental measurements.
- concerning the failure criterion, there is a real challenge to link failure, local stress state and oxidation level in the composite. This work is highly necessary to predict first damage onset in composite structures.
- as far as cyclic thermo-mechanical loadings are concerned, it will be necessary to consider damage propagation, which is rapidly the main and most critical damage process of composite structures.

## ACKNOWLEDGEMENTS

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