

FIRST STEPS OF THE DEGRADATION OF A CARBON/ PHENOLIC COMPOSITE : THE ROLE OF MOISTURE TRANSFER

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Abstract

Carbon/phenolic composites are used as ablative thermal protections in various ultra-high temperature devices (e.g. rocket parts), and the knowledge of their progressive degradation is fundamental in order to design optimized parts.

This paper concerns the very first steps of the material’s thermal history : the initial heating provokes water transfer as well as thermal dilation ; however, by loosing its water, the composite undergoes stress gradients which ultimately lead to cracking.

A multi-scale model featuring heat, mass and momentum transfer has been designed to account for this behavior. It arises that water transfer is fairly complex and requires to separate moisture variables linked respectively to fibers and matrix. In samples containing no temperature gradients, the cracking has been unambiguously related to the parts of the composites where both moisture variables are not in local equilibrium.

Two lines are required after “Abstract”.

1 Introduction

Carbon fibre / phenolic resin composites are widely used as heat shields for atmospheric re-entry of spatial vehicles in severe conditions, *i.e.* Earth or giant planet entry. During their use, these materials have to sustain extreme conditions in terms of thermal fluxes. Because of the very high temperature raise in a short time, the material undergoes severe mechanical and thermo-mechanical changes. In order to forecast the structural and thermal response of the material, it is necessary to upgrade the experimental knowledge and to develop new modeling strategies of the encountered changes. This

work is aimed to help the fabrication and design of thermal protection systems.

Before use, the material is stored in a wet atmosphere for long times and can therefore absorb important water amounts [1,2]; as a result, the thermostructural behavior of the composite depends greatly on this water. During use, the temperature gradient created in the thickness of the material induces three different processes leading to three kinds of structural changes, depicted at fig. 1. The first one is the drying, which induces a particular crack network that will be discussed. Then, the pyrolysis occurs; at that point, the organic resin undergoes thermo-chemical reactions which originates a new family of cracks, while the composite is transformed from its initial C/phenolic state to a C/C material. Finally, the ablation process takes place, consuming the C/C composite on its surface by sublimation and oxidation.

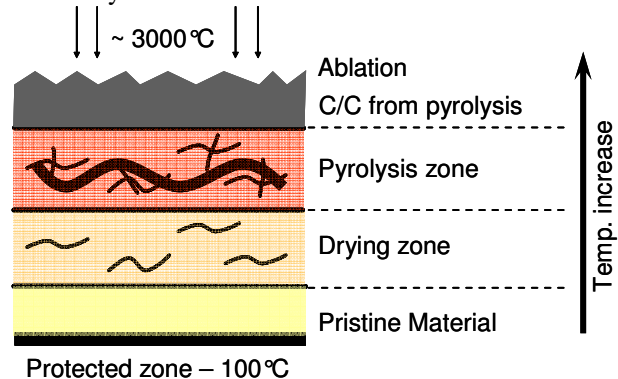


Fig. 1. C/resin composite under high flux

Ablation [3-5] and pyrolysis [2,6-10] processes have been extensively described in the literature, while the drying step has drawn much less attention. The present work focuses on the characterization

and modeling of a carbon/phenolic composite during the first stage of its evolution, *i.e.* the drying.

Previous approaches on this subject [7,11] have reported that moisture elimination requires a vaporization step followed by diffusion or permeation of the vapor through the composite. However the permeabilities measured in the non-cracked specimens lying around 10^{-8} Darcy (or 10^{-20} m²), the related pore sizes would be nanometric ; thus, it is difficult to consider water as a plain gas in such materials. The vaporization-transport model thus has to feature the hindrance by interaction of water molecules with the pore walls, which renders it formally comparable to a solid-state diffusion model. The diffusive transport of water is very slow and strongly activated by temperature, through an Arrhenius-like law.

Recent studies on graphite/epoxy [12] and carbon fiber/epoxy [13,14] composites put the emphasis on the coupling between temperature, moisture content and stresses, occurring through the thermal expansion and moisture expansion coefficients. The internal stresses arising from expansion differences due to moisture gradients or property differences between constitutive phases are appreciable, and may lead to the onset of cracking.

In a first part, the rapid drying of composite samples is investigated, in order to characterize the induced cracking ; then, a model is presented for the simulation of water loss and stress localization, providing possible explanations and criteria for the onset of the first cracks.

2 Experimental characterization of the role of moisture transfer

2.1 Samples and techniques

In order to uncouple partially the intricate phenomena taking place in the material as it is heated, the present approach has been restricted to heating rates and material sample sizes small enough to consider isothermal sample heating as a safe approximation :

$$8a \gg L^2 \frac{\dot{T}}{\bar{T}} \quad (1)$$

(where a is the thermal diffusivity, L the largest sample dimension, \dot{T} the heating rate and \bar{T} the average temperature)

In all cases, the moisture diffusion coefficient D is much smaller than a (ratio from 10^{-6} to 10^{-2} depending on temperature). The sample size has been chosen such that :

$$8D \ll L^2 \frac{\dot{T}}{\bar{T}} \quad (2)$$

This ensures that the transient effects linked to moisture diffusion are clearly observable on the samples. A typical value for L is 5 mm.

The studied material is constituted by lay-ups of woven satin plies, themselves made of carbon fibers ; the matrix is a charged phenolic resin. The fabrics are pre-impregnated with the resin, then cured to allow matrix polymerization.

The samples have been prepared with different initial moisture concentrations by equilibration with atmospheres containing controlled relative humidity (HR) amounts by the method of saturated saline solutions.

The samples have then been characterized by TGA (SETARAM Setsys 1600), which yields the time evolution of the water mass loss, by dilatometry (SETARAM TMA 2400), which gives the time evolution of the sample dimensions, by optical (Nikon Eclipse ME600) and scanning electron (Hitachi S-4500) micrography on polished sections. Finally, mercury porosimetry has been performed on pyrolyzed samples in order to quantify the influence of the water-related cracking on the subsequent phases of the material evolution.

2.2 Results

The first qualitative result of importance is that cracking is observed before pyrolysis only when water is present in the samples, and if the heating rate is high enough.

Choosing a typical heating rate of 40°C/min, the crack development has been identified by micrography. Crack initiation is always the result of matrix-fiber debonding, initially under the form of isolated, elongated pores (fig. 2). They are mainly horizontal on the figure, *i.e.* they are parallel to the plies.

The pores rapidly grow and coalesce into large horizontal cracks with eventually traverse tows along their major elliptic axis (fig. 3). They are always lying well in the middle of the tows ; generally there is only one crack per tow. Their length parallel to the direction of the tows is several millimeters.

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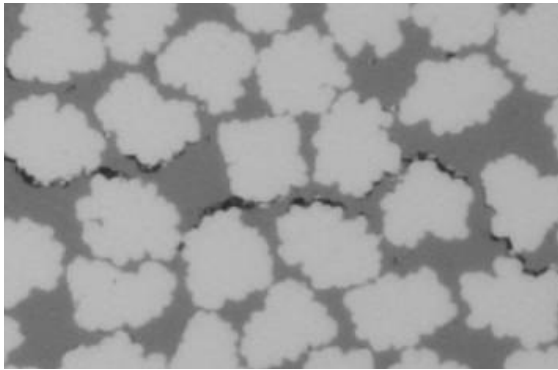


Fig. 2. Initial cracks occur as fiber-matrix debonding (SEM observation)

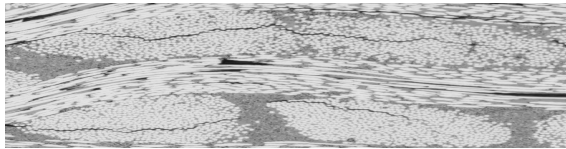


Fig. 3. Optical micrograph of a typical longitudinal crack.

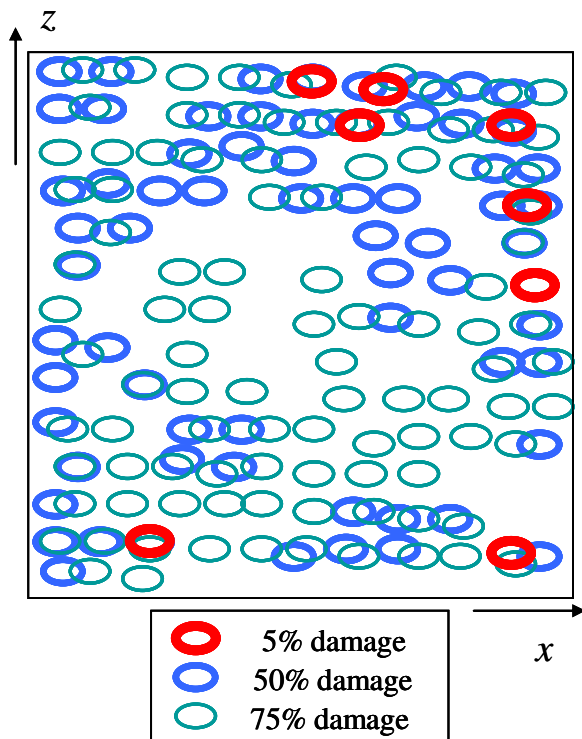


Fig. 4. Distribution of cracked tows on similar samples at three successive heating stages.

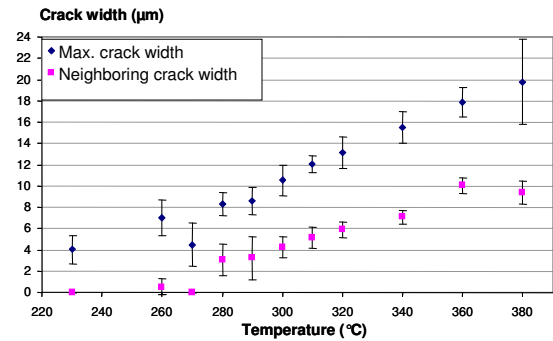


Fig. 5. Crack widths : maximal values and values for the neighboring crack

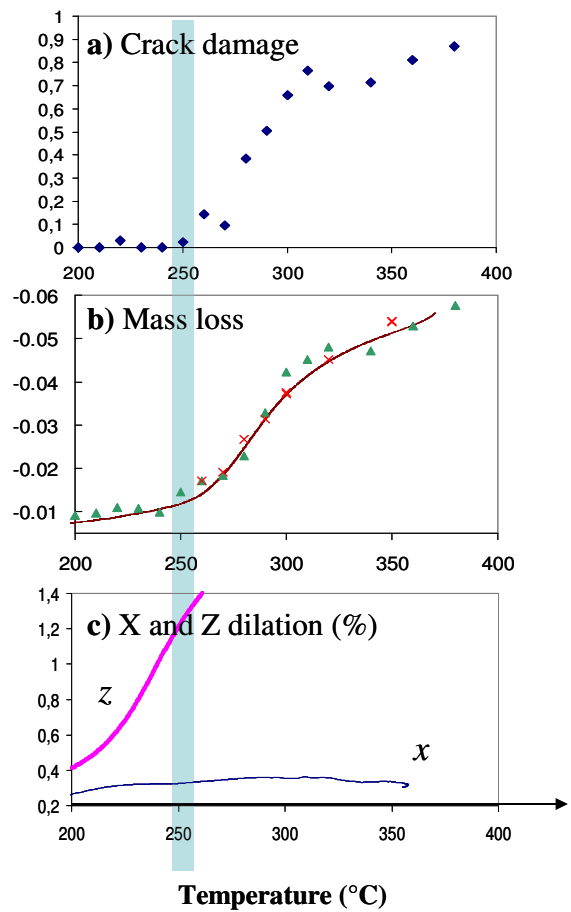


Fig. 6. Evolution with temperature of samples with 5% wt. initial moisture content heated at 40°C/min.
a) Crack damage (fraction of cracked tows) ;
b) Relative mass loss ;
c) Horizontal dilation (%)

The cracked tows are preferentially located at the sample top and bottom boundaries : cracking eventually spreads itself inside the material at later heating stages (fig. 4). When a tow has undergone

cracking, its neighboring tows have a lesser crack opening, as illustrated at fig. 5.

Figure 6 shows the simultaneous evolution of crack damage with mass loss and dilation. Evidently, there is a critical temperature for which cracking appears, which coincides with a sudden increase of mass loss and dilation rate parallel to fibers. It is thus possible to correlate the damage amount with absolute mass loss and with the mass loss rate, itself being linked to the effective diffusion coefficient of water. The onset of cracking leads to an apparent multiplication by 50 of the diffusion coefficient in the damaged zones [15].

Finally, Hg penetration and microscopic observation have confirmed that the dimensions and repartitions of cracks generated by pyrolysis are affected by the presence of the pre-pyrolytic crack family. All the pyrolytic cracks are smaller when pre-pyrolytic cracks have been generated.

2.3 Discussion

From the experimental results, numerous conclusions arise.

Pre-pyrolytic cracking occurs only when moisture gradients are present in the material. Indeed, if there is no water, or if the heating rate is low enough to allow water gradients to lower themselves, no cracking occurs. Moreover, at moderate damage amounts, the cracks are localized in the outer sample regions, where moisture gradients are steepest.

The geometry of the cracks is characteristic either of a vertical traction or of a horizontal compression a tow scale and at fiber scale. This implies the crack nucleation by fiber/matrix interface debonding (since this interface is probably the weakest zone of the composite) and the localization of the cracks along the largest elliptical axis of the tows. One can infer that the stresses are maximal in the center of the tows which are subject to moisture gradients. It is also possible that water vaporization inside the cracks accelerates their growth [11].

The existence of drying cracks increases dramatically the water exchange rate. Moreover, they relax the local stresses : consequently, cracks are less prone to appear close to existing cracked areas. This has a neat impact on the morphological characteristics of the posterior pyrolytic cracks.

The dilation curves show that the vertical dilation is enhanced some 20 to 30°C before cracking, which occurs when the thermal dilation is cancelled out by the horizontal shrinking linked to

water release. The tows are in a state of horizontal compression at that moment. This strongly suggests a scenario for the onset of cracking, that is summarized in fig. 7.

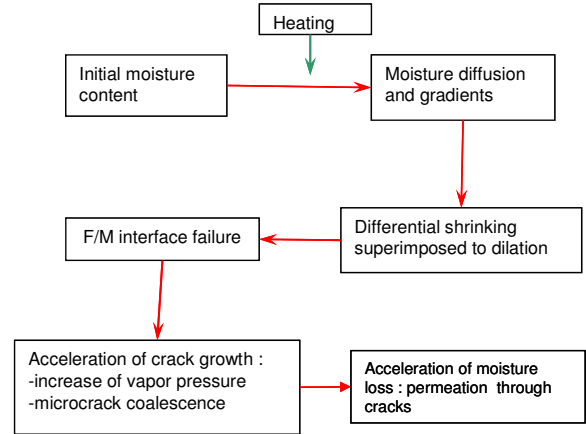


Fig. 7. Scenario of pre-pyrolytic cracking

At this point, it appears that a thermo-hygro-mechanical analysis would help to have a more precise insight on this scenario.

3 Simulations

The next step in understanding the material is to develop and identify models accounting for thermo-hygro-mechanics. Let the question of moisture transfer be treated first.

3.1 “Double moisture”

Clearly, the presence of moisture is the determining factor for this premature damage, so a careful study of water exchange has been performed. Following the “volume averaging” modeling strategy [16], a double change-of-scale approach has been performed ; first from fibers and matrix to average tow properties, and then from average tow and surrounding matrix to global composite properties. It appears that at both scales, one has to consider separate variables describing water activity in all components (fiber, matrix inside and outside tows). A “double-moisture” transfer model, inspired from the “double-temperature” heat transfer problem [9] has the following water balance equations :

$$\begin{aligned} \Phi_1 \frac{\partial C_1}{\partial t} &= \nabla \cdot (\underline{D}_{11} \cdot \nabla C_1 + \underline{D}_{12} \cdot \nabla C_2) + Q_{12} \\ \Phi_2 \frac{\partial C_2}{\partial t} &= \nabla \cdot (\underline{D}_{21} \cdot \nabla C_1 + \underline{D}_{22} \cdot \nabla C_2) - Q_{12} \\ Q_{12} &= a_v h (C_2 - C_1) \end{aligned} \quad (3)$$

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Here, C_i is the water activity in the i^{th} phase, defined by the ratio of the water partial density to the saturation partial density in the same phase, $a_v h$ is a transfer coefficient proportional to the internal interface area a_v (m^{-1}), which is low enough to motivate the separation of the moisture variables C_1 and C_2 , separately averaged over phases 1 and 2 with respective volume proportions Φ_1 and Φ_2 . A criterion for separation is :

$$a_v h \ll \frac{D_i}{L^2} \quad (4)$$

This criterion is well satisfied at all scales and in all directions in the material, as illustrated at fig. 8.

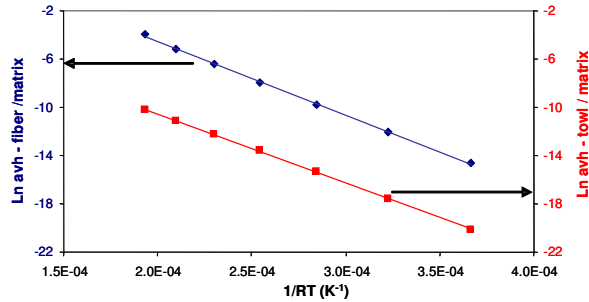


Fig. 8. Moisture exchange coefficient $a_v h$ (s^{-1}) as a function of temperature

For this, it has been necessary to identify all diffusion coefficients for all phases and directions from experimental data, as reported at fig. 9. The striking feature of this graph is that the matrix becomes more conductive than the fibers at high temperature.

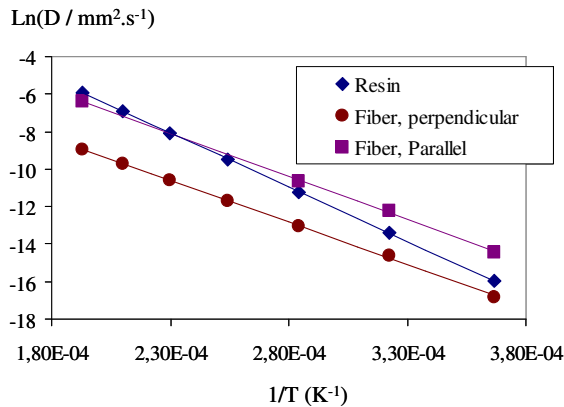


Fig. 9. Diffusion coefficients D ($\text{mm}^2.\text{s}^{-1}$) as a function of temperature for fiber and resin.

As an example of output, fig. 10 is a schematic plot of the relative moisture contents in tow and matrix when cracking begins : a marked difference translates the fact that moisture is evacuated much faster in the matrix than in the tows ; this is also clearly visible at meso-scale, as illustrated at fig. 11.

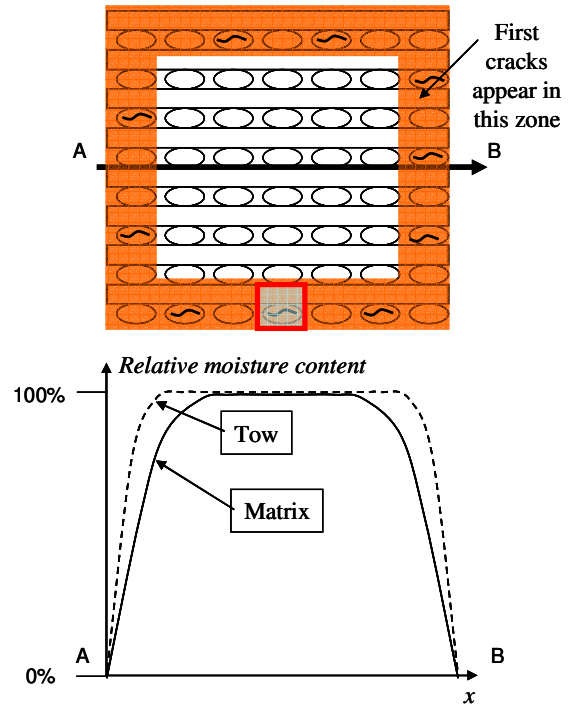


Fig. 10. Above : Sample first stage of degradation under heating and moisture loss. Below : longitudinal profile of moisture content in tow and matrix

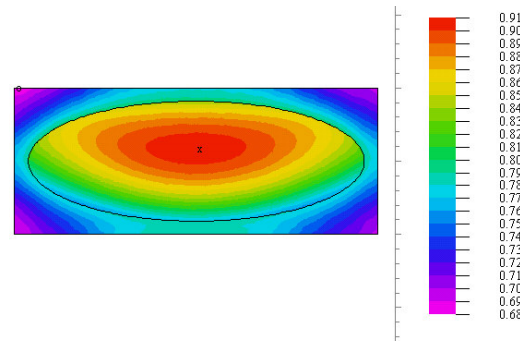


Fig. 11 : Water activity field in a tow located at the bottom of the sample (area outlined in red in fig. 8a).

3.2 Hygro-mechanics with volume thermal dilation

Combining the preceding results with a momentum balance, featuring bulk thermal dilation and moisture-driven shrinkage, one gets an accurate description of the stresses present in the material at macroscale. The key of the mechanism lies in the high-temperature behavior differences between matrix and fibers. When cracking is close to occur, the matrix has a larger diffusivity (and thus a lower moisture amount) and a larger moisture dilation coefficient than the fibers. This yields a larger shrinking effect on the matrix than on the tows. In accordance with this, computations show that the stresses in a tow close to the sample edge and in marked moisture disequilibrium are a compression along the largest, horizontal axis, while vertical stresses are lowest exactly along this axis. This may well favor crack opening in mode I. At microscale, for the same reasons, there is a larger contraction in the matrix than in the fiber : this adds an extra local compression to the global stresses. When the interfacial resistance is passed, then a crack appears ; its propagation is favored by the global stresses.

4 Conclusion

The first steps of carbon/phenolic composite damage during heating have been investigated by various techniques. In samples containing no temperature gradients, the cracking has been unambiguously related to the parts of the composites where the local components are not in local moisture equilibrium. A scenario of crack set-up has been proposed : at moderate temperatures, moisture leaves faster the matrix than the fibers, and the obtained differential shrinking yields compressive stresses on the tows; which eventually lead to crack opening at the fiber/matrix interface. From a modeling point of view, water transfer is fairly complex and requires to separate moisture variables linked respectively to fibers and matrix.

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