EXPERIMENTAL EVIDENCE OF COUPLING BETWEEN MATRIX CRACKING AND OXIDATION DURING THERMAL AGEING OF C/EPOXY LAMINATES

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ABSTRACT

Thermal cycling tests in three environments, neutral (nitrogen) and oxidative (air and oxygen), are performed on 
[0°/90°]_3 carbon/epoxy laminates. Microscopic observations and X radiographs as well as measurements of mass variations of the samples show a significant effect of the oxygen level on the damage development. Important matrix shrinkage is only observed on specimens tested in air and in oxygen, its amplitude depending on the number of the thermal cycles and on the oxygen concentration. Due to coupling between oxidation phenomenon and cyclic thermal stresses an acceleration of matrix cracking process is observed. Moreover, keeping these previously damaged samples 4250 hours at 150°C under 3 bars of air, highlights that the degradation rates as well as the ultimate damage states are depending on the total history of the ageing.

1. INTRODUCTION

In aeronautical applications, carbon/epoxy laminates are widely used when the objective is a significant reduction in weight. In such applications, structures are subjected to mechanical stresses varying during the flight, changes in environment according to altitude and temperature variations. For example, during a flight presenting subsonic and supersonic phases, structural parts can be subjected to cyclic mechanical loading and temperature variations (between -50°C and about 130°C) depending on flight stages, the high temperatures being sustained during the supersonic flight. In composite laminates, because of the strong anisotropy of the thermo-elastic characteristics of composite plies, due to prevented differential expansions the temperature variations, induce laminar stresses that can be very large.

In our laboratory, a battery of thermal cycling tests has been performed previously on various carbon/epoxy laminates in nitrogen, dry air and pure oxygen. The observations made during these experiments have shown matrix cracking to be much more developed in oxidative environment than in nitrogen. Due to thermal cycling, in advanced CFRP laminates, two damage mechanisms are combined: the micro-cracking of matrix, resulting from prevented thermal expansions of the plies and thermal ageing (oxidation and/or thermolysis) [1]. When the thermal variations are cyclic, they induce, at the ply level, cyclic stress variations that can be compared, at this scale, to a fatigue phenomenon. Various types of damage similar to those observed in mechanical fatigue result from these cyclic stresses, namely transverse matrix cracking, fibre/matrix debonding and delamination [2, 3]. When these temperature variations occur in the presence of an oxidative environment, other damaging phenomena appear due to matrix oxidation. Concerning thermoset epoxy polymers, the oxidation phenomenon was essentially studied through isothermal ageing experiments [4, 5]. Some authors have shown that the epoxy-resin oxidation involves a weight loss and a density increase and, as a consequence, shrinkage of the skin layer of the material: a kinetic model of radical chain oxidation coupled with the equation of oxygen diffusion predicts the concentration profile of oxidation products, the weight loss and the shrinkage profiles in a thick block of neat resin...
As a consequence, in thermal cycling in oxidative atmospheres, the coupling between oxidation and thermo-mechanical cyclic stresses accelerates the damage processes of CFRP laminates, all the more as oxygen concentration is high [7]. In literature, most studies relate either to oxidation through isothermal tests at various temperatures and pressures [5, 8] or to fatigue mechanisms [9]. Some studies concerning thermal cycling try to simulate the thermo-mechanical conditions of flight [10, 11] whereas other authors focus on creep phenomenon and the associated predictive models [12]. Up to now, few data are available on the long-term material performances under consideration in such conditions as fatigue, creep and ageing, which are relevant in such a supersonic application.

The results presented in this paper are part of a study supported by the French Research Department and Transport Department within the framework of the “French Supersonic Aircraft Research Program”. The aim of this experimental work is to assess the influence of a preliminary thermal cycling on a following isothermal ageing of a composite material candidate to such application.

2. DAMAGE INDUCED BY THERMAL CYCLING

Experimental conditions

Thermal cycling tests have been performed on continuous carbon fibre and epoxy matrix composites, selected by EADS CCR (Corporate Research Centre -France- of the European Aeronautic Defence and Space Company). The curing process has been optimised in order to obtain a stable material, to avoid any effect of post cure and change of properties during thermal cycling or ageing. Coupons of [0/3/90/3] S laminates have been used, their dimensions were 35×25 mm², the length direction being referred to as the 0° axis. Before tests, the samples have been smoothly polished on two perpendicular sides. They were examined prior to cycling in order to ensure that there were no initial cracks or defects on the free surfaces. The prescribed thermal cycles were triangular, the maximum and minimum temperatures being respectively 180°C and -50°C with constant cooling and heating rates of 4°C/min. To assess the influence of oxygen on material ageing, the tests were conducted in three atmospheres: neutral (pure dry nitrogen) and oxidative (dry air reconstituted from 22% O₂ + 78% N₂, and pure dry oxygen). 500 thermal cycles have been prescribed and, at regular stops, the samples have been removed from the thermal cycling oven to observe damage development by means of optical microscopy, SEM, and radiography.

Damage mechanisms and development

In figure 1 SEM pictures of the free edges of specimens that have experienced 500 thermal cycles in air are shown as an example. Throughout thermal cycling tests performed in oxidative atmosphere (air and oxygen), such observations have shown two types of superficial damages: permanent deformation of the matrix due to its shrinkage and debonding between fibres and matrix (figure 1).

The matrix shrinkage appears on the free edges of the sample as a difference of level between matrix and fibres and is visualized as dark and deep hollows, imprinted on the initial plane of the polished edge. Moreover, the wider the matrix areas concerned, the deeper the hollows. Such damage mechanisms do not exist when thermal cycling tests are performed in nitrogen as can be seen in figure 2, in which SEM pictures obtained after 500 thermal cycles in nitrogen and in air are compared.
Throughout the tests, the matrix shrinkage was observable on all the surfaces of the specimens, but such observations did not allow specifying if its “depth” varies according to the time of ageing. In order to measure the depth of these residual deformations of the matrix, an optical profiler was used (WYKO NT1100 from Veeco). Thanks to this optical interferometer associated to a motorized stage for measurements over a larger field of view, quantitative results were obtained and processed statistically. For each experimental condition, about 150 measurements have been performed on three different specimens. As an example, all the data collected on specimens subjected respectively to 100, 300 and 500 thermal cycles in air are gathered in the frequency distributions shown in figure 3.
One can see in this figure that the shapes of the three distributions are similar: they are not gaussian, the lower depth values being quite more frequent than the greater ones. However, as the number of thermal cycles increases, the peaks of the distributions present a progressive shift towards higher depth intervals and the extent of the depth values concerned increases. Measurements of matrix shrinkage depths have been done for specimens tested either in nitrogen, or in air, and oxygen. The statistical results obtained from the depth distributions are collected in table 1 for comparison.

Table 1: [0\(_3/90\_3\)]\(_s\) laminate, statistical values of matrix shrinkage depth according to the number of thermal cycles (-50°C/180°C) and the test environment

<table>
<thead>
<tr>
<th>Number of thermal cycles</th>
<th>NITROGEN</th>
<th>AIR</th>
<th>OXYGEN</th>
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<tbody>
<tr>
<td></td>
<td>500</td>
<td>100 300 500</td>
<td>100 300 500</td>
</tr>
<tr>
<td>average (µm)</td>
<td>0.18</td>
<td>1.15 1.75 2.2</td>
<td>1.6 1.87 2.25</td>
</tr>
<tr>
<td>standard deviation (µm)</td>
<td>0.08</td>
<td>0.57 1.04 1.11</td>
<td>1.06 1.11 1.43</td>
</tr>
<tr>
<td>extent (µm)</td>
<td>[0-0.4]</td>
<td>[0.4-4] [0.4-5.5] [0.4-6]</td>
<td>[0.4-7] [0.4-7.5] [0.4-8]</td>
</tr>
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</table>

One can see in this table that the mean “depth” value measured on flat surfaces of specimens submitted to 500 thermal cycles in nitrogen is very low (0.18 µm), the extent of the distribution being less than 0.4 µm. Such values can be considered equal to those obtained on the initially polished surfaces. Comparatively, the mean shrinkage depths measured on specimens tested in oxidative environments are much higher: after 500 cycles performed in air or in oxygen, the mean values are close to each other and more than ten times higher than in nitrogen (~2.2 µm). Moreover, the mean depth values increase with the number of cycles, and are systematically higher in oxygen than in air. The same remarks can be done about the values of the standard deviation and extent of the frequency distributions, showing that this damage mechanism is only significant in oxidative atmospheres and all the more as the oxygen concentration is high.

In accordance with the epoxy-matrix oxidation model presented elsewhere [6], these types of damages, absent when tests have been carried out in nitrogen, could be induced by the oxidation process which is very active above 120°C in air and in oxygen. When matrix shrinkage occurs (i.e. in oxidative environment), the high strain gradients present in matrix areas, close to fibres which have a very high stiffness, lead to high local stresses that can be favourable to debonding between fibres and matrix or/and to crack initiation as shown in figure 1.

As the test duration increases, one can observe on the edges of the samples that these short micro cracks grow through the layer thickness and develop as “transverse cracks”: these cracks span the whole thickness of the inner or external layers and increase in number with the number of thermal cycles. Moreover, they propagate from the edges of the specimens towards the core of the laminate. An example of such development of cracking is given in figure 4 in which three X-radiographs obtained after 100, 300 and 500 thermal cycles in air are shown.

These pictures show that, in air, the first transverse matrix cracks appear in the internal layer at 100 cycles, that after 300 cycles, some are present in the external layers too and that 500 thermal cycles induce a very developed matrix cracking in every layer of the [0\(_3/90\_3\)]\(_s\) cross ply laminate. At the end of the test, transverse cracks are well distributed in the length and width of the coupon. The cracks present in the external layers span the whole sample length, while, in the inner layer, the crack length does not exceed half the specimen width.
Examples of X radiographs of samples subjected to 500 thermal cycles, either in nitrogen, in air or in oxygen are given in Figure 5. The matrix crack accumulation and growth are very different according to the gaseous environment of the test: no or very few and short cracks are observed in samples tested in nitrogen, whereas they are numerous and long when the tests are performed in air or in oxygen. Moreover, the matrix cracking appears more developed in oxygen than in air: the cracks are more regularly distributed in the whole coupon, and some local delamination between external and internal plies can be observed at high magnification.

**Weight loss**

In agreement with the literature, when our composite samples are subjected to thermal cycling under oxidizing atmospheres, the high temperatures involve a thermo-oxidation of the matrix. This phenomenon of thermo-oxidation affects primarily the external surfaces of the samples and might induce a weight loss of the specimens. This variation of mass is, for a long time, taken into account as an indicator of the degradation of the composite material. In this section, we present gravimetric follow-ups of the samples throughout thermal cycling tests. The samples are weighed at each test interruption and the obtained relative mass loss values ($\Delta M/M$) are gathered in figure 6, against the number of thermal cycles.

For each experimental condition, we have observed that the experimental curves describing relative weight loss present a rapid decrease during the first 25 first cycles, identical in air and oxygen and probably corresponding to a phase of residual drying. Then, the relative mass variations of the coupons decrease regularly, the variations appearing linear with the number of cycles. Surprisingly, the thermal cycling in neutral atmosphere induced some weight loss, which is, however, less than that observed in air and in oxygen. In agreement with some authors [13, 14], the weak but continuous mass loss observed in nitrogen could be due to a thermolysis of the matrix occurring at the highest temperatures of the thermal cycles. In order to compare the oxidation level of the samples according to the type of atmosphere, air or oxygen, it appeared necessary to exclude the mass loss due to both the residual drying and the thermolysis phenomenon. We then calculated the differences between the mass variations measured during tests in oxidative environment and those obtained in nitrogen, in the linear
part of their evolution. From these values, we deduced the rates of these relative mass losses (per cycle), which are collected in table 2.

![Graph showing relative mass variations](image)

**Figure 6:** [0\(^{y}/90\(^{y}\)]\(_{8}\) laminate, relative mass variations of specimens vs the number of (-50°C/180°C) thermal cycles for three different environments.

One can see in table 2 that the thermal cycling in oxygen induces a higher level of degradation than the thermal cycling in air, the mass loss rate being about 2.8 times higher than in air.

<table>
<thead>
<tr>
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<th>Relative mass loss rate (/cycle)</th>
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<tr>
<td>air-nitrogen</td>
<td>(0.90^{0.55} \times 10^{-6})</td>
</tr>
<tr>
<td>oxygen-nitrogen</td>
<td>(2.50^{0.45} \times 10^{-6})</td>
</tr>
</tbody>
</table>

**Table 2:** [0\(^{y}/90\(^{y}\)]\(_{8}\) laminate, (-50°C/180°C) thermal cycling, relative mass loss rate (/cycle).

### 3. ISOTHERMAL AGEING OF DAMAGED SPECIMENS

In a second step, the previous specimens, damaged by 500 thermal cycles in different atmospheres, have been exposed in isothermal conditions at 150°C under 3 bars of air. The test continued 4250 hours, and the weight variations of the specimens were measured. In order to evaluate the loss of weight of a virgin specimen subjected to such an isothermal ageing, we used an oxidation kinetic model established successfully to predict the degradation of the neat epoxy matrix [1] and of UD composite specimens [15, 16]. Figure 7 presents the relative variations of mass against the ageing time: the predicted weight loss is represented by a full line and must be compared to the experimental measurements which concern the initially damaged specimens. One can see in figure 7 that the experimental values obtained for the three specimens are very close from each other till around 1500 hours. Moreover, they correspond to the values predicted by the model for a virgin specimen: this correspondence might be explained by the low sensitivity of this global degradation parameter, inadequate to detect the small mass variations which occur during the first hours of isothermal ageing. Beyond 1500 hours of ageing, the decrease in specimen weight varies like the initial damage state: the higher the initial cracking, the faster the degradation process. In that range, the
relative mass variations of the damaged specimens deviate increasingly with time from the values expected for a virgin sample. At the end of the test, after 4250 hours of isothermal ageing, the relative weight loss of the specimen initially subjected to 500 thermal cycles in oxygen is more than 3 times higher than that predicted for an undamaged sample...

**Figure 7:** Relative mass variations of \([0_3/90_3]_s\) laminates initially damaged by 500 thermal cycles and exposed 4250 h at 150°C under 3 bars of air.

In order to emphasise these differences, we calculated the mean rates of weight loss in a time range longer than 1500 hours using the approximation that the relative mass variations evolve linearly with time of ageing. In table 4 the values of these degradation rates (per hour) are given for the different considered specimens. The comparison of these mass loss rates put in light the great influence of the initial damage state of the specimen on its further response to the oxidation process. Even the specimen previously tested in nitrogen, which had only few and short cracks before the isothermal ageing, presents an increase of mass loss rate when the test duration exceeds 1500 hours. This acceleration is more pronounced for specimens first tested in air and in oxygen, which were more damaged and hence, presented greater surfaces reactive to oxidation.

**Table 3:** Comparison of the relative mass loss rates (/h) due to an isothermal ageing (4250 hours, 150°C, 3 bars of air) for \([0_3/90_3]_s\) specimens initially submitted to 500 thermal cycles and for a virgin sample (simulation).

<table>
<thead>
<tr>
<th>Relative mass loss rate /hour</th>
<th>Virgin specimen (simulation)</th>
<th>Prior thermal cycling in nitrogen</th>
<th>Prior thermal cycling in air</th>
<th>Prior thermal cycling in oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7×10^{-6}</td>
<td>1.25×10^{-6}</td>
<td>1.8×10^{-6}</td>
<td>2.1×10^{-6}</td>
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</tbody>
</table>

X-radiographs of the three specimens have been taken at the end of the isothermal ageing test (after 2450 hours) and are compared in figure 8 to the initial X-ray pictures obtained at the end of the 500 thermal cycles. One can see in that figure that the isothermal ageing in air induced an important increase of damages. Because the initial damages were very small in the sample first tested in nitrogen, the X-ray picture shown in figure 8a/ is typical of the damages
induced by an isothermal ageing: in the internal layers we observe very numerous short cracks and local delaminated areas close to the edges of the sample whereas cracks appear evenly distributed in the external layers. Moreover, one can see some internal cracks that developed from the longest external cracks, probably open enough to permit the diffusion of air. The pictures shown in figures 8b/ and 8c/ put in light a correspondence between the initial cracking pattern and the ultimate one. The initial crack array can be recognised, the cracks appearing longer and wider open, and surrounded by very numerous short cracks distributed all through the plies. The differences in cracking density mentioned after the thermal cycling between specimens tested in air and in oxygen persist; the last samples appear as the most damaged.

**Figure 8:** X-ray pictures of \([0_3/90_3]_3\) coupons
LEFT: after 500 thermal cycles (-50°C/180°C), a/ : nitrogen, b/ : air, c/ : oxygen
RIGHT: PLUS 4250 h of isothermal ageing in air, (150°C, 3 bars)
This comparison between the initial damage states and the ultimate ones clearly shows that there is a coupling between the matrix cracking and the oxidation processes: each cracked surface is a new site for oxidation which favours the cracking process and so on... it leads to a damage state all the more developed as the specimen was previously damaged. These observations roughly explain the comments we made about the specimen weight measurements: because of this coupling, the degradation state of a specimen, (characterised in that study by the crack distribution and by the relative weight loss of the sample), strongly depends on the history of its ageing.

4. CONCLUSION

The experimental conditions of this study have been designed in order to put in light the coupling between cracking and oxidation mechanisms of epoxy matrix composite laminates subjected to thermal cycling or isothermal ageing tests.

In a first part, [0°/90°]s coupons experienced 500 thermal cycles (-50°C/180°C) either in nitrogen, air or oxygen atmospheres. Microscopic observations and profile measurements have shown the presence of matrix shrinkage on samples tested in oxidative environment: this phenomenon has been related to an oxidation process depending on the test duration as well as on the oxygen concentration. The sample mass losses measured during those tests have been found as high as the oxygen concentration is important, which confirms the preceding interpretation. Moreover X-radiographs have shown the influence of the environment on matrix cracking, which appeared more developed in oxygen than in air and practically absent in nitrogen.

At the end of the thermal cycles, the same specimens have been subjected to an isothermal ageing in air. Comparison of mass variations and X-ray pictures taken at the end of the test highlighted a coupling between matrix cracking and oxidation processes, the degradation rates as well as the ultimate damage states depending on the total history of the ageing.

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REFERENCES