DURABILITY EVALUATION OF CARBON/BMI COMPOSITES AFTER THERMAL AGING

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Keywords: *Organic Matrix Composite, Isothermal Aging, Supersonic Aircraft Transport*

1 Introduction

1.1 Context

This article synthesizes all the results obtained during the French-Japanese cooperation on the supersonic aircraft transport – under the SJAC-GIFAS Frame Agreement – and concerns the durability evaluation of Carbon/Bismaleimide (BMI) composites after thermal aging. The long-term behavior is a major topic to use composite materials such as aircraft structures over twenty or thirty years in service-life. New organic composite materials can satisfy these requirements but they must undergo physical and mechanical tests to be qualified.

1.2 Objectives

Durability aspect of organic composite materials is a very complex problem since it comprises multi-disciplinary effects coming from various and numerous factors such as temperature, pressure, oxygen, moisture, radiation, polluted volatiles as well as mechanical stresses in service-life. In standard applications, structural composites evolve in air for flight time and the two main aging factors are heat and oxidizing atmosphere. Actually, we are dealing with a combination between temperature and oxygen effects. This combination gives rise a damage which is a consequence of chemical and physical aging undergone by the organic matrix. Consequently, to meet the problem on durability, it is necessary to appeal both physics of polymers and mechanics of composite materials. The aim of this research program is to value the physical and mechanical properties taking into account damages occurring under various thermal conditions in order to predict the long-term behavior.

2 Work program

2.1 Materials

The carbon/BMI composite laminate is a typical example of composite systems to study durability although other thermoset resins such as epoxy or polyimide resins are suitable too, depending of their long-term heatproof capacity. Two kinds of composite laminates from the same BMI family have been selected: the first one is MR50K/2020 system (Mitsubishi Rayon Ltd); the second one is IM7/M65 system (Hexcel Composites) (see manufacturers data in Tables 1 and 2).
The different laminates lay-ups were manufactured as listed in Table 3. A modified quasi-isotropic composite was studied using 24-ply laminates with a stacking sequence of $[(+45/-45/90)_3/(0)_3]_s$ for fracture toughness (DCB) tests; 8-ply laminates with a stacking sequence of $[+45/-45]_{2S}$ for off-axis tensile tests, a quasi-isotropic (QI) composite was studied for non-hole (NHC) and open-hole (OHC) compression tests and a 8-ply unidirectional laminate for weight loss and damage assessment.

2.2 Aging conditions

The aging has been carried out by isotherms selected within the glassy state of the resins (Tg~270°C for both BMI selected resins) but above their maximal use temperature (about 120°C at Mach 2). Isothermal conditions in air have been performed at 150, 180 and 200°C for several thousands hours (from 1,500 up to 10,000 hours) at each temperature and for both composite materials. Therefore, each thermal condition is like an accelerated artificial aging with high temperature and short time intended to reproduce use conditions on long-term applications. The selected moderate thermal conditions should insure the validity of this equivalence [1].

MR50K Carbon Fiber Properties	Strength	5500 MPa
	Modulus	295 GPa
Prepreg Properties	Fiber Area Weight	145 g/m^2
	Resin Content	34 %
Cure Cycle		180^{o}C/6 hrs
Post Curing Condition		240^{o}C/6 hrs

Table 1. Manufacturing data for MR50K/2020 composites.

IM7 Carbon Fiber Properties	Strength	5480 MPa
	Modulus	276 GPa
Prepreg Properties	Fiber Area Weight	134 g/m^2
	Resin Content	35 %
Cure Cycle		190^{o}C/4 hrs
Post Curing Condition		245^{o}C/6 hrs

Table 2. Manufacturing data for IM7/M65 composites.

Test	Lay-up
Toughness (DCB)	$[(+45/-45/90)_3/(0)_3]_s$
Tensile (Off-axis)	$[+45/-45]_{2s}$
Compression (NHC & OHC)	$[+45/0/-45/90]_{4s}$
Damage assessment	$[0]_8$

Table 3. Composite laminates manufactured with both prepregs.

2.3 Testing

Different physical and mechanical testing have been performed before and after aging, in order to follow the evolution of mechanical properties with aging time and temperature and describe the physicochemical degradation.

The mechanical characterization is performed by fracture toughness tests at a macro-scale on DCB specimens and off-axis tensile tests on $[+45/-45]_{2S}$ laminates. Moreover, the compressive strength of non-hole (NHC) and open-hole (OHC) $[+45/0/-45/90]_{4s}$ QI specimens is determined for each thermal aging condition defined at the three temperatures. For compression testing, only the holes are machined before aging on different laminated plates cut from the original quasi-isotropic panel. These plates are aged under the different conditions (temperature and aging time) and then the specimens are cut inside each plate. By this way, only thermal degradation inside the hole and on the laminate surfaces is taken into account (no free-edge effects due to degradation of the specimen edges). All the mechanical tests are performed at room temperature.

The physical tests consist on following the glass transition temperature (*T*g) and measuring the weight loss evolution on UD specimens. The identification of the chemical structure and its modification on the two composite laminates is performed by IR analysis. The material degradation is assessed by microscopic observations at macro- and meso-scales by light and electron microscopy.

3 Physical tests results

3.1 Matrix thermostability

Fig.1 shows the weight loss during aging. The weight decreases by isothermal aging at any temperature. The amounts of weight loss are almost same between both laminates. The weight losses are clearly related to the aging temperature. It seems caused by accelerated diffusion of oxygen through the surface, where the matrix is degraded by the thermo-oxidation reaction [2].

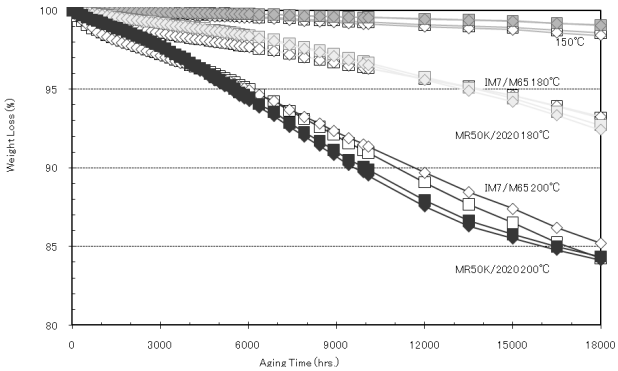

Fig.1. Weight loss during aging.

3.2 Network stability by DMA

The glass transition temperature (*T*g) is evaluated using Dynamical Mechanical Analyzer (TA Instruments Q800 DMA) to understand polymer network stability (chain cutting and cross-linking combination) every scheduled aging time at each aging temperature. Fig.2 shows the *T*g evolution after aging. The *T*g was monotonically increased with aging time, the degree of evolution is significant in higher aging temperature. The increase seems to be brought about by what is called post cure effect, which is a further enhancement of cross-

linking density due to the reaction of remaining functional groups.

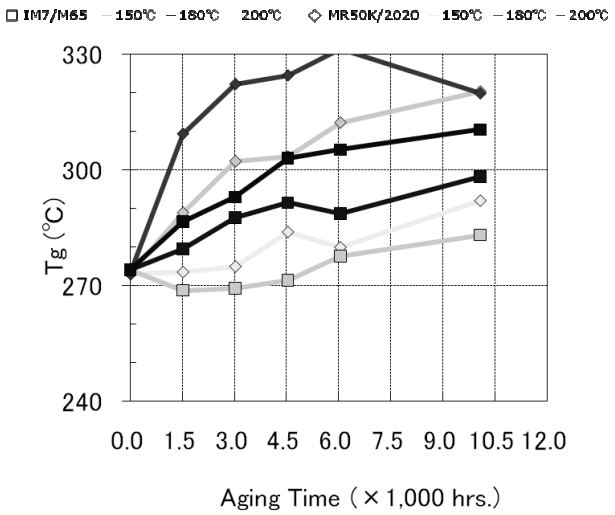

Fig.2. *T*g evolution after aging.

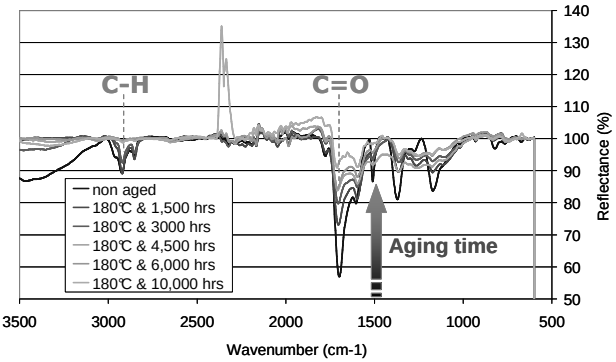

Fig.3. IR spectrum evolution after aging at 180°C (MR50K/2020 UD composite on its free surface).

3.3 Chemical stability by IR spectra analysis

It is not an easy task to obtain IR spectra of good quality on specimens' surfaces due to the local degradation caused by the thermo-oxidizing effect itself. It was observed no significant changes in IR spectrum in the core material, realized after cross section of the aged specimen, for any temperature and any time of aging. For the IM7/M65 material the surface of the specimens was too rough to obtain correct IR spectra (roughness due to the peel-ply coming from the manufacturing). On the contrary, for MR50K/2020 system, with a smooth surface, IR spectrum evolution has been measured (see for instance Fig.3). For the three temperature of aging, we can observe a progressive decrease of characteristic absorption peaks corresponding to oxidative sites (C-H links at about 2,870 cm^{-1}) or oxidation products (C=O links) with aging time. This evolution is linked to a consumption of the matrix by thermo-oxidation reaction. The chemical degradation of the matrix by isothermal aging seems to remain at the surface of the material.

4 Mechanical tests results

4.1 Fracture toughness

The strain energy release rate *G*Ic was calculated from the results of Mode I loading DCB (Double Cantilever Beam) tests according to JIS K 7086 method (Japanese Industrial Standards). Fig.4 shows the *G*Ic evolution after thermal aging. The GIc dramatically decreased when aged at 150°C up to 1,500 hours and are not related to the aging temperature. Over 6,000 hours the *G*Ic values do not meaningfully reflect the interlaminar toughness degradation because propagation of the delamination between other layers was prominently generated during testing. Significantly the delamination propagated near surface. Therefore, the delamination seems to be propagated by accelerated diffusion of oxygen through surface. However, it is not fully understood why there is no big difference among aging temperatures.

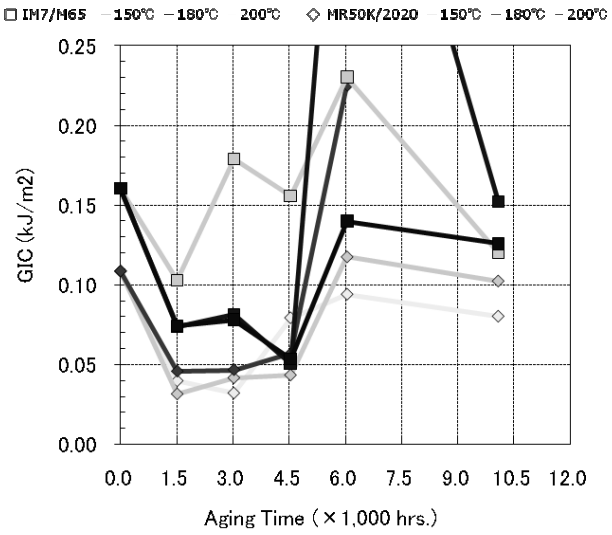

Fig.4. *G*Ic evolution after isothermal aging

4.2 Off-axis tensile tests

The matrix rigidities were evaluated by measuring the in-plane shearing modulus during simple off-axis tensile tests of 8-ply laminates with a stacking sequence of $[+45/-45]_{2S}$ and performed according to JIS K 7073 method. The modulus and failure strain were measured by strain gauges. Fig.5 shows the modulus after thermal aging. The modulus decreases slightly by aging time. The trend of modulus decreasing is related to the aging temperature, but the effect is not so big.

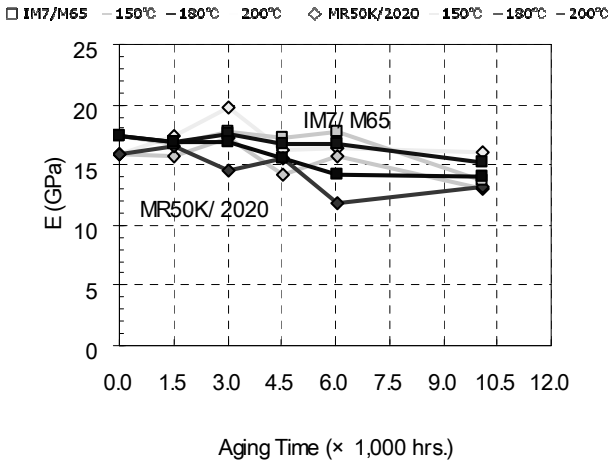

Fig.5. Off-axis tensile tests modulus evolution after thermal aging

4.3 Compression testing

On Fig.6 & Fig.7 are depicted the non-hole and open-hole compression strengths evolutions of a QI laminate as a function of aging time and temperature for the two materials. Each strength value is a mean value of several compression tests (2 NHC and 4 OHC) with indication of standard deviation. The results indicated at time "0 hour" correspond to reference values without any aging.

This evolution is roughly the same for both materials with a slightly decrease of compression strength with temperature and aging time. The decrease is more severe for aging temperature of 200°C, particularly for MR50K/2020 material after 4,500 hours of aging time, which corresponds to the degradation of the first 0°-plies (second ply), as can be seen on the microscopic observations (see Fig.10 in section 5).

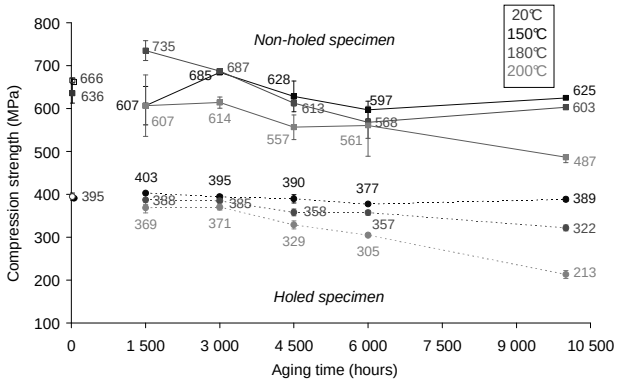

Fig.6. Compression strength evolution after isothermal aging (IM7/M65 material).

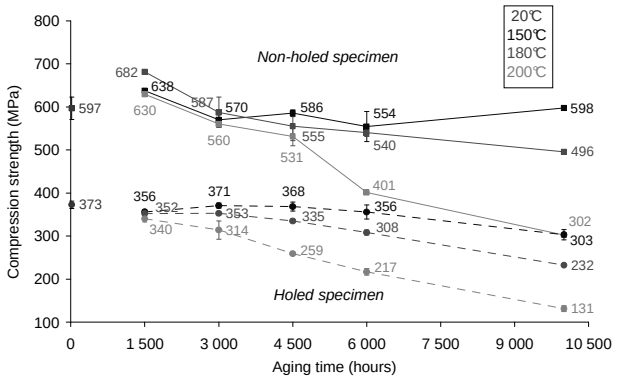

Fig.7. Compression strength evolution after isothermal aging (MR50K/2020 material).

5 Damage assessment after isothermal aging

To analyze the damage due to thermo-oxidation effect, examinations by light and electron (SEM) microscopy have been carried out on polished free edges and cross-sections of specimens (at 7 mm from the free edge perpendicular to the fiber direction) cut from unidirectional composite panels before aging. It's worth noting the IM7/M65 UD panel is a 30 plies laminate (only 8 plies for MR50K/2020).

Like seen on Fig.8 – representing the microscopic views of free edges after aging for one material – a special pattern of microcracking appeared, sooner with higher temperature and with an increasing crack density as a function of aging time. Both materials are nearly affected with the same damage state.

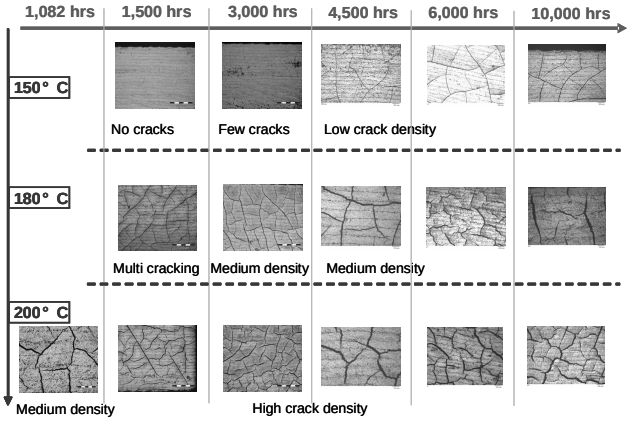

Fig.8. Microscopic observations on the free edges of aged UD specimens (IM7/M65 material).

SEM observations of both aged materials show some micro damages like fiber/matrix debonding, matrix microcracking, and even a superficial shrinkage of the matrix between fibers (Fig.9). Of course after 10,000 hours aging the cracks are longer and larger than those after 4,500 hours aging and, in an equivalent manner, with increasing aging temperature.

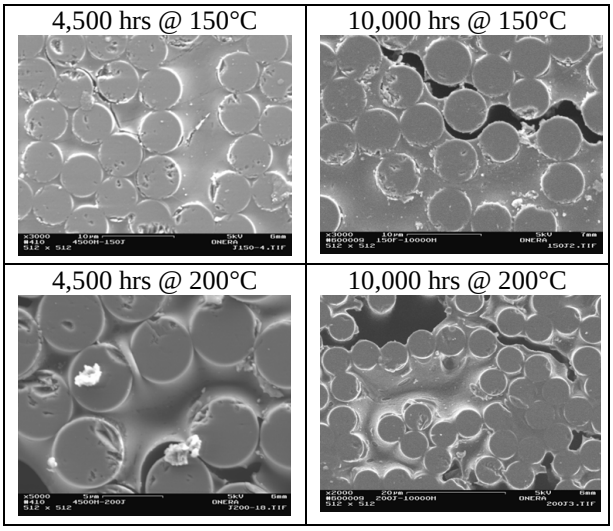

Fig.9. SEM observations on free edges of aged UD specimens (MR50K/2020 material).

In fact these damages are only developing inside an "oxidized area" formed at the surface of the aged material because no evidence of these damages can be seen in the core material, as seen in the cross sections reported in Fig.10. All the transverse cracking vanishes inside the material, whereas we can observe a darker zone near all the free surfaces corresponding to the degradation of the matrix by thermo-oxidation reaction. The thickness of this oxidized layer is depending of the aging temperature and time. In this layer with weaker resin, the cracks are more likely to be initiated and develop under the combination of chemical degradation of the matrix and its physical shrinkage. Up to 4,500 hours of aging, only the outermost ply of the laminate seems to be affected by this degradation. After 10,000 hours of aging, the second and even the third ply can be degraded, mainly at 200°C aging temperature (Fig.10). It's probably why the compression strength results are more affected under these aging conditions (see Fig.6 & Fig.7), considering the second ply of the QI laminate is a 0°-ply (see Table 3) which ensures mainly the strength of the whole laminate (in this case, two 0°-ply upon four are affected by thermal aging).

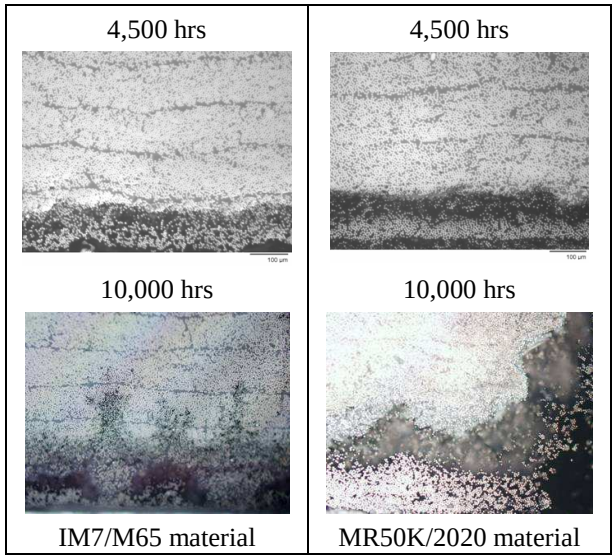

Fig.10. Microscopic observations on the cross-sections of aged UD specimens at 200°C.

Concerning compression test specimens, considering the free edges are cut after aging of panels, the only area affected by the thermal aging are hole's edge and free surfaces. Only these areas have to be taken into account in the aging influence on compression strength evolution. Fig.11 shows evidence of the surface oxidized layer in cross sections near the hole of quasi-isotropic open-hole compression specimen. We can observe the thickness of the oxidized layer depends also on the fiber orientation: more this

orientation is perpendicular to the free edge (arrow) more the oxidized layer is thick.

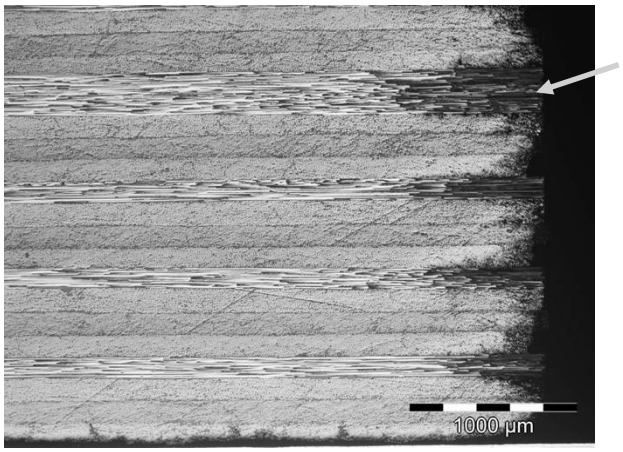

Fig.11. Microscopic observation on cross-section near the hole edge of QI specimen aged at 200°C up to 1,500 hrs (MR50K/2020 material).

6 Conclusions & perspectives

In the present work, two carbon/BMI systems have been selected for their good long-term behavior at intermediate temperatures (supersonic flight conditions). Different composite laminates have been manufactured and the work program has included mechanical characterization, physicochemical degradation assessment and damage observations on different laminate lay-ups.

Concerning the compression tests, the failure strength decrease is clearly related to the degradation due to thermo-oxidation effect. The decrease is particularly pronounced at highest aging temperature and for aging times that correspond to the degradation of the first 0°-plies, as can be seen on the microscopic observations. In the oxidized area, the matrix is degraded by the thermo-oxidation reaction, as shown by IR analysis but also by the corresponding decrease in weight evolution. As a consequence, in this brittle layer of matrix, some micro cracking appears easily like some fiber/matrix debonding or matrix cracks (SEM observations) and can propagate to form transverse cracking at the ply-scale (microscopic observations) but always near the free surfaces. No evidence of cracks inside the laminates has been shown. In the particular case of aged DCB specimens, some longitudinal cracks (in the 0°-plies) may have been created during aging under constant residual stresses condition. The toughness of the composites have significantly degraded properties in the first aging time probably due to post cure effects (the cross linking density increase but the brittleness of the matrix too) as shown by the *T*g evolutions for the same times. The re-rising of *G*Ic values for longer aging times is more related to multiple damages formed during testing that contribute to the energy absorption by a significant fiber bridging. At last, the off-axis tensile modulus is slightly affected by the thermal degradation but with a constant decrease versus time.

In this study, some relationships between damage and respective residual mechanical properties have been established for two carbon/BMI systems. Some issues remain, in particular the shared role between thermal aging effects, residual thermal stresses and mechanical loading. This is the object of the next French-Japanese cooperation project.

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