AGEING QUALIFICATION RULES FOR AERONAUTICAL MONOLITHIC COMPOSITES

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ABSTRACT

Structures are exposed to a series of events including loading, damage and environmental threats. These events, either individually or cumulatively, can cause the structural degradation.
Current economic conditions require the use of most aircraft beyond their original design service objectives. The durability of composite materials involves complex phenomena, at the molecular scale, that can induce modification of their mechanical properties. The establishment of criteria and models allowing predicting the long-term behavior of composite structures is an important challenge for aircraft manufacturers and authorities. The optimization of the performance of structure components and thus of the materials, on longer operating lives, need to have robust prediction models, that consider the total of the applied stresses and external environmental threats. An extensive survey have been undertaken to intent to identify and condense what has been, thus far, discovered as the effects of ageing on polymeric composites. Special emphasis was placed on epoxy matrix reinforced with carbon or glass fibers composites. That includes environmental effects and prediction methodologies (accelerated methods and analytical models). The next objective is to do the parallelism between the academic research studies and the OEM (Airbus collaboration) practices. The final objective is to conclude on a “conservatism assessment” of industry practices versus academics ageing studies for composites.

1 INTRODUCTION

The long-term performance of composite under specific conditions requiring 30-50 years of service life is, in general, not known nor well understood. To promote wider industrial usage of composite, the critical issue of long-term durability of composite must be addressed.
Aging is defined as the effect, on materials, of exposure to an environment for a period of time; the process of exposing materials to an environment for an interval of time [6].
Composite material components are subjected to a wide range of environments. The operating conditions in which the aircraft must perform are not well characterized. Environmental factors of major importance include a combination of humidity and temperature. Many studies have been conducted to investigate moisture absorption as well as the reduction of mechanical properties due to temperature and moisture exposure.
One of the most important requirements of a structural polymer is its ability to retain a significant proportion of its loadbearing capability for long periods of time under diverse environmental conditions. Therefore, there is an understandable urgency to better understand the effects of aging on composite polymers.
The current approach used to account for environmental factors is to define exposures that are extremes and selectively evaluate by test the effects on material properties. These extremes are then considered to be invariant during the lifetime of the structure. Strength values are reduced to coincide with the environmental extremes.

2 ENVIRONMENTAL THREATS

Composite structures are sensitive to the environment. The main identified environmental threats of composite structures are:

- Temperature
- Humidity
- UV radiation
- Loads
- Impacts
- Service fluids
- Chemical environment
- Lightning strike
- Galvanic corrosion
- Erosion, weathering
- Fire

2.1 Temperature and moisture

Composite materials can absorb part of the ambient environment humidity[13]. This may cause a loss of mechanical properties and has therefore to be quantified. That is why some specimens are exposed to “wet conditioning” to get the composite to absorb humidity and are tested in a so-called “Hot-Wet” condition.

Moisture

On the solid laminate itself, the identified environmental effects of moisture are [1][10]:

- Moisture pick-up, with reduction of the matrix governed strength properties (compression, bearing, interlaminar strength). This strength reduction is enhanced by elevated temperatures.
- Reduction of the matrix glass transition temperature
- Very little effect on stiffness properties.

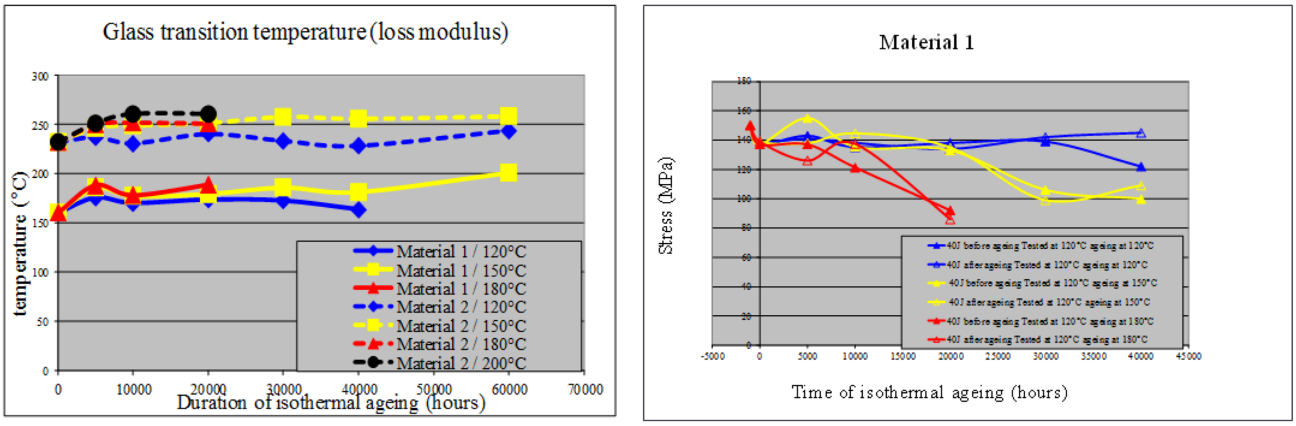

Figure 1: Glass transition temperature and stress evolution during thermal ageing [8]

On integrated metal parts (like fasteners):

- Galvanic corrosion, mainly with aluminium in contact with carbon-epoxy, very critical in salt atmosphere.

Some examples of moisture and temperature effects on thermoset laminates are [12]:

- Humidity effect on a laminate is assumed to be reversible (and asymptotic)
- Combining most adverse conditions in terms of humidity and temperature may lead to laminate property static strength reductions in the range of: -5% to -15% for a 180°C curing system. The assumed maximum temperature in operation is 75 to 80°C.
- Only matrix governed properties are under concern (compression, shear, bearing).

The glass transition temperature (Tg) for epoxy resin composite the Tg is for Cycom 977-2, 138°C dry condition and 104°C wet condition. The glass transition concerns the amorphous phase and has a key role on polymer properties [2].

To better assess and predict the water ingress in the composite laminate, the need of modelling has been raised. One of the satisfactory assumptions is to assume that water diffusion in the composite complies with the same laws than heat conduction – Fick's second law [3].

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2}$$

With D: Diffusion coefficient (m^2/s)

c: molar concentration ($mole/m^3$) at t

$$D = D_0 e^{-\frac{E}{RT}}$$

The characteristic time diffusion is 8 days for 1mm and more than 2 years for 10mm[9].

The humidity absorbed by a composite complying with a "Fickian" behavior[4], depends on:

- The material itself
- The laminate thickness
- The relative humidity
- The ambient temperature

In steady conditions, the equilibrium moisture content depends mainly on the material itself and the relative humidity. This content is slightly dependent on the temperature.

It has been observed that the absorption reached a maximum level, called "saturation", which depends on different parameters:

- The relative humidity of the environment
- The matrix type of the composite
- The fibers/matrix ratio

The time needed to reach this level depends on different parameters:

- The thickness (the thinner, the quicker it saturates)
- Temperature of the environment (the hotter, the quicker it saturates)
- The relative humidity of the environment (the higher, the quicker humidity is absorbed).

Temperature

For subsonic aircraft, except local effects (like turbine exhaust), the maximum expected temperature is reached on ground condition and depend on:

- The solar radiation
- The sun position
- The solar reflection provided by what surrounds the structure
- Paint colour properties (absorptivity and emissivity)

- The ambient temperature
- The cooling effect during taxiing, taking off and climbing.

The maximum assumed values are [11]:

- For Airbus programs: ISA + 40°C → 55°C (131°F)
- FAA recommendation: 51°C (124°F)

This temperature will not be exceeded 99.9% of the time at hot dry climates (Desert valley, Sahara).

Tests

To analyse the effect of moisture in the strength caracteristics of a composite part, it is usual to introduce the maximum expected moisture content in the test article [5]. The recommended procedure is:

1st: To establish, for the selected composite material:

- Its equilibrium moisture content in a RH=85% steady environmental condition. This content will be referenced as the 'Material Target Moisture Content' MTMC. This content must be calculated with respect to a fully dry situation that means established from pre-dried coupons. Knowing that this moisture content is more or less affected by the conditioning temperature, select a conventional conditioning temperature of 70°C (usual value in European certifications).
- The maximum laminate thickness expected to reach the equilibrium level within the aircraft lifetime (value dependent on the diffusivity and the average ambient temperature). A 8mm thickness, exposed on both faces, has been accepted for Airbus certifications.

2nd: To manufacture, in the same shot as the test article, travelers coupons representative of the same composite material and stacking sequence as the test article. Typical traveler size: 100x100mm, two travelers per composite material and representative thickness. In Airbus, the traveler size is usually: 75x75mm.

3rd: When starting the accelerated ageing, to introduce half of the travelers (one of the two identical ones) in the same conditioning chamber and start immediately to dry the remaining half part in order to establish the initial moisture content at the beginning of the conditioning.

4th: To monitor, through successive weightings, the traveler moisture pick-up and stop conditioning when the material target moisture content is reached by the maximum thickness traveler (but not more than the thickness expected to reach equilibrium before the end of lifetime).

The moisture content of the structure to be considered as reference should be equivalent to the equilibrium level of the material system typical for 20 years of operations under worst environment conditions (70°C / 85%HR) [6]. The saturation under those normal conditions is what was agreed by the manufacturer and the authorities in order to demonstrate the resistance of the aircraft structure under worst operating conditions.

The mechanical property degradation due to humid ageing depends on the material moisture content only regardless the thermohygrometral history (mission profiles) having led to that content. It is why the maximum composite moisture content at the end of lifetime is to be established.

Accelerated wet conditioning:

The usual test is not normal wet conditioning experienced in service but accelerated wet conditioning. The normal accelerated wet conditioning terms are 70°C and 85%HR. The test specimens are put in the climatic chamber together with the traveler specimens with one put in the oven for drying. Regularly the traveler specimens are weighed. The saturation level is defined in percentage of the dry mass. The wet conditioning is finished when the saturation level is reached.

For practical reason, it is interesting to reduce the conditioning time by:

- Increasing the relative humidity (from 85% to 95% HR or more): Quite usual. It is then recommended to end the conditioning by a steady phase at 85%HR in order to homogenize the through-the-thickness moisture content.
- Increasing the conditioning temperature: the recommended maximum values are in Europe, 70°C and in the USA [6]: 82°C. A too elevated temperature may modify the chemistry of the material which will be

no longer representative of the component in service, and/or introduce post-curing effects, hidden by the mechanical properties degradation.

The aged specimens are then tested during wet aging, before or after depending on the mechanical test: Impact, fatigue, rupture, multiphase test sequence, equipment.

For wet conditioning under both normal and accelerated conditions, the specimens are removed out of the wet ageing process when the equilibrium condition is reached [5]:

$$\frac{m_{j-1} - m_{j+1}}{m_{j-1}} \leq 5 \times 10^{-4}$$

The mass m represents the mean weight of the wet traveler specimens at the time t.

There is more tests with composite materials than for metals because:

- There is a low accessibility to calculation then need to generate design values through complex test articles
- Are sensitive to environment, and then need to duplicate some tests in order to derive the ageing related knock down factors.
- There is a material anisotropy, then need to increase the test matrix at the coupon level to investigate various stacking sequences.
- There is a higher mechanical property variability than for metals, then need to increase the sample size in order to lower the knock down factors imposed in the derivation of the allowables.

Ageing is taken into account through the induced degradation due to moisture ingress. The design level precautions taken are:

- Design values and allowables are generated allowing for most adverse conditions
- Fatigue is commonly demonstrated with a structure at least representative of a minimum aged condition (60% of the moisture content target).

Some in –service inspections have been implemented:

- For solid laminate: no control is possible
- For sandwich parts: zonal, NDT, tap—chick and ultrasonic methods are used.

Solid laminate parts have, so far, demonstrated a good behavior in regard to humid ageing. Sandwich parts proved to be more questionable in this respect.

The approach for design purposes regarding environmental sensitivity in terms of moisture and temperature is to assume a worst case as presented above. If the material is assumed to be fully saturated and at the maximum temperature, material allowable can be derived for this extreme. This is a conservative approach, since typical service environments do not generate full saturation for most complex structures. Once the diffusivity of a composite material is known, the moisture content through the thickness distribution can be accurately predicted by Fickian equations. This depends on an accurate characterization of the temperature-humidity service environment.

2.2 UV radiation

UV rays from the sun can degrade epoxy resins. This is easily protected by a surface finish such as a coat of paint. The need of adequate protection for composite structures is required to prevent irreversible material degradation. Unacceptable, irreversible degradation of CFRP parts by UV-radiation shall be fully avoided by use of temporary protection or by other adequate systems providing UV-resistance during manufacturing process and transport up to their assembly on the final aircraft and operation. Composite surface protection and activation covers UV sensitivity and related ageing effects. It has been demonstrated throughout several independent studies that all A/C structure FRP materials suffer from UV.

Like Humans, Polymers and organic compounds and suffer from UV.

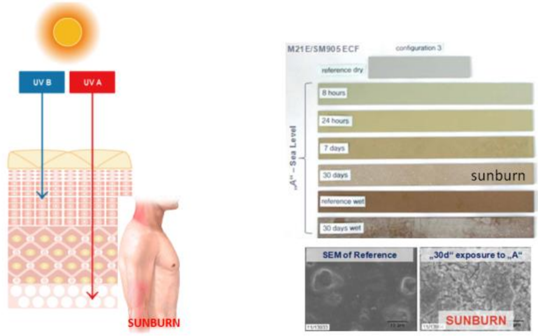

Figure 2: UV influence and degradation on organic compounds

The typical stages of FRP material degradation triggered by UV are:

- Loss of surface smoothness
- Fading
- Embrittlement
- Crack initiation/formation
- reduction of thickness
- Increase in Tg
- Loss of mechanical performance

It is a surface degradation, the effects are limited to surface, thus it is mainly a concern for paintings.

In order to assess the level of degradation following scenarios are to be tested in order to ensure that the material is capable to provide sufficient protection against UV degradation for production and in-service related aspects. The tested methods are:

- Natural exposure: two scenarios, one for aircraft in operation (cruise altitude UV exposure) and the other one for aircraft manufacturing chain (sea level UV exposure). The scenarios take into account all important influencing factors e.g. UVA/UVB range, moisture, latitude, albedo, ozone column,…
- Artificial exposure: The tests shall be conducted with adequate equipment for artificial UV aging. UV exposed samples shall always be compared to both reference configurations at delivery state (directly after cure, dry) and after exposure to humidity (wet).

The reference is the maximum solar insolation for the critical wavelength portion 300-400nm on ground which corresponds to locations in Spain in midsummer (June/July) taking into account latitude and altitude. For flight level exposure an intensification factor of 2.1 has been developed (Airbus source).

All test results are displayed for all material configurations analyzed are conducted per following scheme:

1. Receiving inspection / Visual analysis after exposure
2. Micrographic analysis
3. SEM analysis
4. In-plane shear
5. 3-point-bending

In respond, in-service limitations related to UV exposure times of FRP components depending on component condition are published for the A/L by the manufacturer.
Example:

1. Aircraft storage outside only with primer surface treatment: 60 days maximum allowed exposure time
2. Aircraft flying only with primer surface treatment: 30 days
3. Aircraft outside only with surface film: 60 days
4. Aircraft flying only surface film: 30 days
5. Bare FRP – no surface treatment / protection: not allowed
6. Bare FRP after lightning strike: 50 flight cycles

2.3 Corrosion, chemical and biological attacks

Another feature of composite that is related to environment is resistance to corrosion. FRP composites (exception of some carbon/bismaleimides) are immune to salt water and most chemical substances as far as corrosion sensitivity [7]. Indeed, organic matrix composites are totally insensitive to corrosion; however, galvanic corrosion may be generated on the metal parts which are in contact with them. Carbon fiber is cathodic, aluminum and steel are anodic. This carbon in contact with aluminum or steel promotes galvanic action which results in corrosion of the metal. In respond, the design level precaution is the use of interposition (insulating) materials (like fiberglass, mastic, putting) and in-service inspection. Corrosion barriers (fiberglass, sealants) are placed at the interfaces between composites and metals to prevent metal corrosion. Anoter precaution regards the use or paint strippers around most polymers. Chemical paint strippers are very powerful and attack the matrix very destructively. Chemical paint stripping is forbidden on composite structure.

Biological attack on composites may consist of fungal growth or marine fouling. As reported in the literature, fungal growth does not appear to be as damaging as the wet conditioning that promote growth. Fungicide has been mixed with the resins to retard this growth.

2.4 Service fluids

The aircraft fluid environment consists of fuel, hydraulic fluid, lubricants, deicing compounds and water. A study of stressed and unstressed composite materials evaluated short-beam shear strength and tensile strength after immersion in fuel, hydraulic fluid, a fuel-water mixture and fuel/air cycling for 5 years. The fuel-water immersion appeared to be the most damaging, reducing the tensile strength of graphite/epoxy specimen by 11% and short-beam shear strength by as much as 40%.
Mechanical testings are performed to assess effect of fluids (under specific conditions) by the manufacturer. Effect is compared to humidity aging and potential knock down factor are considered.

2.5 Fire

Fire, smoke and toxicity are checked through established standards. The application of material is done where appropriated (emphasis in the passenger area).

2.6 Erosion

Another factor is erosion or pitting caused by high speed impact with rain or dust particles. This is likely to occur on unprotected leading edges. There are surface finishes such as rain erosion coats and paints for preventing surface wear.

2.7 Lightning strike

Lightning strike is also a concern to composites. A direct strike can cause considerable damage to a laminate. Lightning strike protection in the form of conductive surfaces is applied in susceptible areas. In cases where substructure is also composite, the inside end of attachment bolts may need to be connected with each other and to ground by a conducting wire.

3 CONCLUSION AND DISCUSSION

Aging ability of a composite part is driven by the presented environmental factors. These environmental factors are design variables. They are today characterized by a deterministic approach in the industry. The applied approach defines a worst case value to meet in the design and certification of the aircraft. This brings to specify a safety factor which allows covering unknowns. This approach thus introduces conservatism. Indeed the application of a factor of safety (or knock-down factor) may be too large. This approach had worked will in the past. Indeed it is a robust approach demonstrated with no in-service issue regarding aging on monolithic composite parts on more than 230 million flight hours (26000 years). Since the introduction of advanced composite materials in aircraft, design difficulties appeared like material strength degradation to elevated temperature, absorbed moisture, impact damage or hidden damage. This strength reduction factors have been taken into consideration for the design by developing worst case scenarios and assume their existence for the life of the part. These factors are variables and treated as constants. The approach is highly robust and safe but can lead to an over conservatism.

Composite part design is governed by compounded conservatism coming from worst case criteria like: loading x safe factor (1.5), worst case temperature, moisture, damage, undetected and material allowables defined from statistical criteria. The risk of combining these conservative structural criteria is a loss in the product efficiency.

The question of a probabilistic approach is thus arisen. The characterization will be statistical and may provide a desired reliability in the design.

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