EFFECTS OF PHYSICAL AND CHEMICAL AGING ON STRENGTH AND BEHAVIOR OF CARBON/BMI COMPOSITES FOR SST STRUCTURES

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Abstract

Organic composite structural parts for Supersonic Transport (SST) applications are subjected to both mechanical stresses and various environmental conditions. The damage analysis quickly becomes complex with the number of parameters to be combined and needs particular investigation means. Aging factors alone can lead to various damages within the composite materials. Through the difficult problem of combined effects from all aging factors it is interesting to analyze the effect of temperature and oxidizing atmosphere in conjunction with the mechanical properties. For isothermal conditions, there exists different outward signs of aging close to free surfaces of the composite but also in the volume of the composite. Surface aging is induced by thermo-oxidation which gives rise to microcracking and acts on failure stresses of the composite. The thickness of the oxidized layer can be determined by optical examination and modeling. In the bulk of the composite, volume aging primarily modifies the mechanical behavior of the composite laminates. Within the matrix, the chemical and physical evolution of the resin network is represented by a displacement of the glass transition temperature which constitutes an internal variable that can be integrated into a multi-scale mechanical model.

1 General Introduction

Whatever the company interested in supersonic air travel, important scientific and technological advances have to be done to insure the development of a viable SST for aircraft manufacturers and air-carriers. A large number of new technologies take their source in work developed by research institutes when their laboratories are tuned on needs expressed by industry. Issues raised by the supersonic transport concern a large range of scientific disciplines offering numerous research topics in challenging areas. In certain key areas such as structural materials, research does condition the success of an eventual vehicle. Progress accomplished on composite laminates has a direct impact on lightweight and performance of structural parts of the vehicle. However, to answer the questions asked by industrial partners concerning durability and reliability of these materials, it is necessary to investigate their properties throughout their aging. Carbon fiber/organic matrix composites have great potential as light structural materials for long term use.

Within the general term "durability" there is a combination of mechanical and physico-chemical effects responsible for the life time of the composite materials [1]. Particularly, damage is a main consequence of the physical and chemical aging undergone by the organic

matrix. Physical aging modifies the space organization of macromolecules without changing the chemical composition of the backbone. Chemical aging modifies the chemical structure of the backbone through various mechanisms such as reticulation, depolymerization, elimination and substitution. Aging occurs by apparent degradation such as oxidation, corrosion and microcracking as well as through invisible damage within the chemical network such as chain cutting. The problem is complex because numerous aging factors and time are involved [2] and it is very difficult to reproduce and manage realistic test conditions in the laboratory. For example, it is not reasonable to consider thermal aging tests as long as 100 000 hours for a SST vehicle. As a consequence, an accelerated artificial aging performed in laboratory is intended to reproduce practical use conditions and adds a further level of complexity to the problem [3].

Thus, there is such a range of interlinked parameters that analytical methods for assessment of properties on the long-term become unreliable. The ideal situation would be to consider each aging aspect and then combine them one by one to give the most accurate prediction of the real behavior of the composites. This task is gigantic. To day, mechanisms of aging due to each parameter taken individually are still so poorly understood that the structure-properties relationship have not yet been established.

Without additional mechanical load, effects of aging factors can lead to stresses causing damage in the whole of the composite. Main aging factors are temperature, oxygen, pressure, radiation and atmospheric products such as ozone, humidity, carbonic or sulfur gas and volatile pollutants. In ordinary applications, structural composites evolve in air. In this case, we are dealing with a combination of temperature and oxygen effects. Degradation occurs differently on free surfaces or close to the surface and in the bulk of the composite. In any rigor, to account for the elementary mechanisms of degradation, analyses of the surface and of the internal volume must be made on composite materials subjected to isotherms or thermal cycles of long times. Tests must be also carried out for measuring residual mechanical properties. To meet this investigation, it is necessary to appeal to both physics of polymers and science of composite materials. This paper does attempt to give some elements of response.

2 Materials and Processing

Organic matrix composites based on high glass transition temperature polymers are likely to be considered as the materials of structural parts for next generation aircraft. Thermoset resins such as epoxies or polyimides are often selected as matrices subjected to exposures in air at moderate temperatures (up to 120°C) during several thousands hours. Typical examples are given by aircraft manufacturers for certain body parts of future supersonic vehicles particularly close to engines. As an example, the selected composite system consists of T800H carbon fibers from Toray Industries, Inc. and bismaleimide resin from Hexcel Composites. This bismaleimide resin (BMI) is prepared by blend of aromatic bismaleimides and diallyl bisphenol A derivative with 20% of linear polyimide (in which the nature is not revealed by the supplier). Composite laminates with different lay-up and neat resin plates were processed by compression molding under the same conditions and then post-cured under primary vacuum in accordance with the cure cycle recommended by the supplier (140°C/1h/0.6MPa+190°C/4h/0.6MPa followed by post-cure at 245°C/6h). The fiber volume content is estimated to be 60% approximately and the glass transition temperature determined by Dynamical Mechanical Analysis (DMA) is about 250°C.

The composite laminates and neat resin plates were machined to specimen sizes suitable for various mechanical tests and microscopic examination. Thermal aging was carry out in ovens for several thousands hours at various temperatures selected within the glassy state such as 120, 150, 180, 210 or 240°C. A great quantity of specimens were removed from ovens at well-defined exposure times for

mechanical tests and examination. Most samples were previously polished on free edges before thermal aging. Then some samples were cut and their cross-sections were polished in order to examine degradation in the bulk of the composite. For most mechanical tests, sample free edges were removed to avoid the edge effects (edges often damaged and not representative).

3 Experimental Data

As an example, figure 1 shows compressive strength after isothermal aging of a quasi-isotropic (QI) carbon fiber/BMI composite.
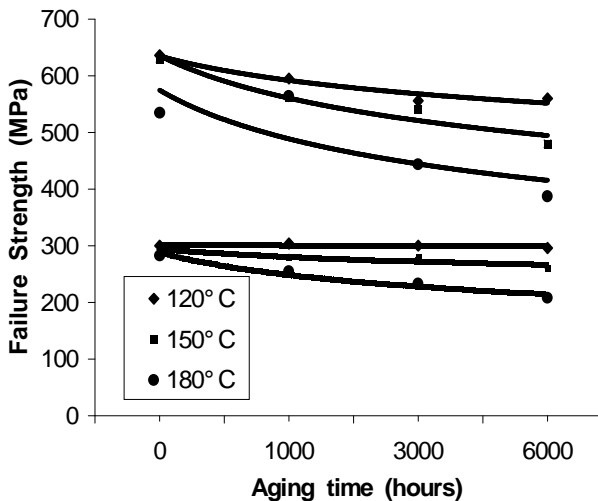

Fig.1. Compressive strength versus aging time of unnotched (upper curves) and open-hole (lower curves) specimens from QI T800H carbon fiber/F 655-2 BMI resin composite.

For each temperature and whatever unnotched or open-hole composites are, the failure strength decreases monotonously against the aging time. This decrease mainly depends on load transfer from fiber to matrix. The load transfer is directly linked to the health of the organic matrix and is therefore depending on the chemical structure of the BMI resin during thermal aging. By determination of weight loss, figure 2 highlights degradation during thermal aging particularly severe at 180°C and figure 3 shows the corresponding damage consisting of transverse and longitudinal cracks in a 0° ply observed on free edges of coupons.
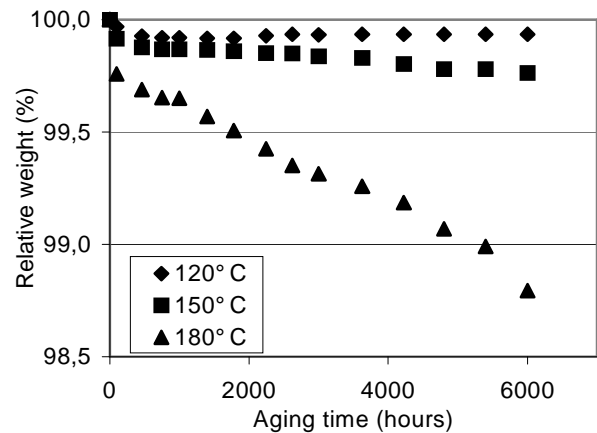

Fig. 2. Weight loss versus aging time at three temperatures for a QI carbon fiber/BMI resin composite.

Fig.3. Damage observed on 3 plies of a [+45/0/-45/90]4s QI carbon fiber/ BMI resin composite after aging at 180°C/6000 h. Only 0° ply is microcracked.
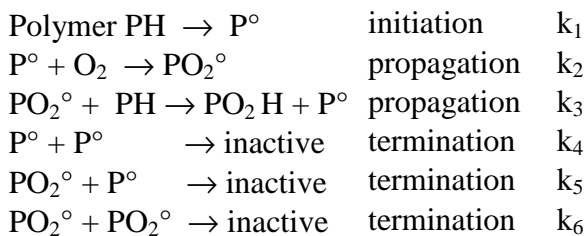
3. Discussion and Correlation

In the present case for study, composite laminates are primarily subjected to temperature and oxygen. Effects of these two factors, alone or combined, give rise to complex damage kinetics [4]. Only for the effect of temperature (e.g. aging in neutral gas), one must expect a physico-chemical evolution of the whole matrix of the composite. With additional oxygen, the thermo-oxidizing effect will lead to damage on the surface of composite laminates following a specific degradation mode.

3.1 Surface Aging

Surface aging is concerned with a small oxidized layer which rarely exceeds 0,5 mm even under severe conditions. To form this oxidized layer, oxygen diffuses into the resin and reacts with the macromolecular structure. The reaction-diffusion process can be formulated using a modified Fick's diffusion law and a kinetics of decomposition of the structure as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - r(\,C\,) \qquad (1)$$

where C is the oxygen concentration, D, the coefficient of diffusion, t, the time, x, the abscissa (normal to the surface) and r(C), the oxygen consumption rate. The mathematical form of r(C) is derived from a realistic mechanistic scheme within a closed loop describing a set of radicalar reactions (initiation, propagation, termination) with respective rate constants, k_i [5] :

Polymer PH $\rightarrow$ P°	initiation	k_1
P° + O$_2$ $\rightarrow$ PO$_2$°	propagation	k_2
PO$_2$° + PH $\rightarrow$ PO$_2$H + P°	propagation	k_3
P° + P° $\rightarrow$ inactive	termination	k_4
PO$_2$° + P° $\rightarrow$ inactive	termination	k_5
PO$_2$° + PO$_2$° $\rightarrow$ inactive	termination	k_6

After some manipulation of kinetic expressions

$$\frac{\partial C}{\partial t} = D_i\frac{\partial C}{\partial x_i^2} - k_2 C\left[P^\circ\right] + k_6\left[PO_2^\circ\right]^2 \qquad (2)$$

where i = 1, 2 or 3 indicates principal directions in the composite, P° and PO$_2$° are given as functions of oxygen concentration C [5].

The distribution of oxidation products through the thickness of the material is given by

$$Q\left(x_i, t\right) = \int_0^t r(\,C\,)dt \qquad (3)$$

The numerical resolution of equation (3) gives access to the thickness distribution of oxidation products and its evolution [6]. The main mathematical and physical consequence of the expression (1) form is the appearance of an oxidized layer at the polymer or composite surface when C is high enough. Figure 4 schematically shows oxidation profiles through the thickness of the material and also the oxidized layer thickness defined by (OLT), ½ Qs(t). In general case, the calculated values are relatively well close to data measured by light microscopy [7]. Interference contrast used with a light microscope allows easily to determine the oxidized thickness.

A steady state is generally reached in the kinetic process and the oxidized thickness tends towards an asymptote as defined in figure 4 by ½ Qs(t). However, during an isotherm, the degradation of the material continues issuing in a phenomenon of almost imperceptible ablation of the surface. In addition, a model of weight loss given by [8] is directly comparable with experimental thermo-gravimetric data such as given in figure 2.
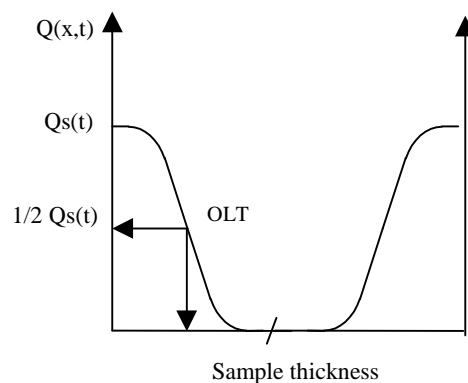

Fig.4. Oxidation profile through a sample thickness

By oxygen diffusion and whatever the nature of the polymer matrix is, it is clearly established that the structural changes occurring within the oxidized layer give rise to embrittlement at two levels. At a molecular scale, there is a combination between breakage and crosslinking of chains. These effects modify the chemical structure of the polymer network. If the chain fracture is predominant then strength and strain to failure decrease within the oxidized layer. Further, mechanical properties such as toughness are affected in the whole of the composite. At a macroscopic scale, after an induction period, the oxidized layer exhibits weight loss but becomes denser at the same time. This leads to a light compaction of the oxidized layer generating tensile stress state both between fibers and between OLT and intact core. Thermo-oxidation and stress intensity are responsible for the occurrence of multiple microruptures and then by coalescence to microcracks in the oxidized layer. Further, when oxygen penetrates inside microcracks, then microcrack sides are surrounded by a new oxidized layer. Thus, there is a propagation of the microcrack by progression of the brittle oxidized layer [9]. Generally created next to fiber/matrix interface, most microcracks generates transverse or longitudinal cracks such as seen in figure 3. The extent of cracking depends substantially on the fiber direction. It is easier to propagate along fibers (0° orientation) than in the direction 2 or 3. In these cases, the respective damaged zone is less deep because the crack propagation is reduced by the perpendicular fibers. Subsequently, damaged zones are confined near the free surfaces. Finally, although oxidation occurs as a fine layer everywhere on the surface of the composite, it represents a dominating factor for initiating microcracks and thus plays a role in failure properties. Figure 5 shows effect of surface protection to avoid oxidation. By comparison with the unprotected composite B, only the protection D improves the average compressive strength. For the others cases, protections do not prevent oxygen diffusion [10]. About the case D, if all surfaces would have been protected by the BMI resin, strength
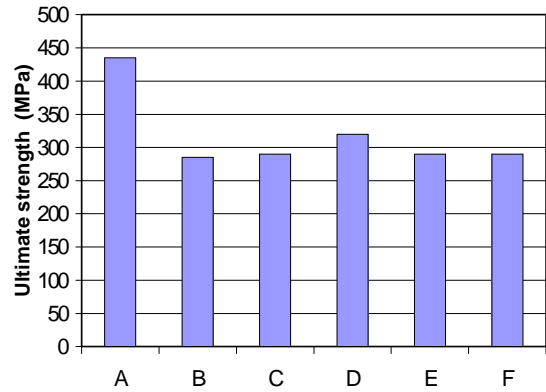

Fig. 5. Effect of oxidation resistant treatment on the open–hole compressive strength of carbon fiber/BMI resin composite after aging for 5,000 h at 180°C . A : no aging, B : unprotected, C : hole bolted, D : hole and free edges sealed by a BMI resin, E : full surfaces painted by silicon and F : surfaces covered by a glass fiber cloth.
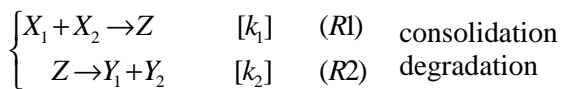
value would be higher although, as foregoing above, direction 2 of composites does not present a deep oxidized layer. More likely, the gap between values A and D appeals to both surface aging and volume aging in the bulk of the composite.

3.2 Volume Aging

While thermo-oxidation concerns sample surfaces, temperature affects the whole of the composite. For applied temperatures, thermal aging produces many changes that modify failure properties and viscoelastic behavior of the matrix. For example, there exists mechanisms leading to phase separations since the BMI matrix is consisted of thermoset and thermoplastic phases [11]. In addition, there exists thermal stresses between plies of the QI composite [e.g.,12], fiber/resin interface damages [13], size effects [14]. All these changes take part in the decline of mechanical properties. It seems that the primary factor is the physico-chemical modification of the matrix. During thermal aging, chemical effects produces a combination of degradation and consolidation in the matrix structure. First, temperature causes consolidation by an increase of the crosslink density due to extended post-

cure. Then, consolidation is combined with degradation coming from a thermolysis effect. This one breaks polymer chains and creates free radicals which can themselves lead to reorganization [15]. If the chain failures are more numerous than the new links of the network, mechanical properties tends to decline. Concerning only physical aspect, over long aging times, thermal stir is weak but the network evolves nonetheless to a more stable state because the configuration entropy of chains decreases slowly and the free volume tends towards a homogeneous distribution.

The evolution of the glass transition temperature, Tg, gives a method to follow volume aging. Although this includes the whole of the matrix, the contribution of the thin oxidized layer can be neglected. At first time, the temperature consolidates the matrix (similar to a long post-cure), then Tg must increase. In a second stage, degradation dominates consolidation then Tg must decrease. Kung *et al* give an expression of the evolution of Tg according to the aging temperature and time [16]. Now, to describe a consolidation-degradation process, it is possible to introduce a physico-chemical variable representing a crosslink density with the following mechanistic form [17]

$$\begin{cases} X_1 + X_2 \to Z & [k_1] \quad (R1) \quad \text{consolidation} \\ Z \to Y_1 + Y_2 & [k_2] \quad (R2) \quad \text{degradation} \end{cases}$$

$$k_i(T) = A_i \exp\left(-\frac{E_i}{RT}\right) \quad i = 1,2 \qquad (4)$$

where Z is the result from the combination of entities X_i as well as the decomposition of entities Y_i. k_1 and k_2 are reaction rates following Arrhenius' law. The crosslink density τ_R is taken as proportional to Z [17] and then

$$\frac{d\tau_R}{dt} = \frac{k_1(T)}{(k_1(T)t+1)^2} - k_2(T)\tau_R \qquad (5)$$

To connect the crosslink rate to the glass transition temperature one can use a simplified form of Di Marzio's relation [18]

$$Tg(\tau_R) = Tg_\infty - cTg_\infty^2 (1 - \tau_R) \qquad (6)$$

where Tg_∞ is the glass transition for a crosslink saturation and c a constant. Evolution of Tg on aged BMI resins has not still established but as an example on an epoxy resin also used for SST applications, figure 6 shows a relationship between glass transition temperature and aging time.
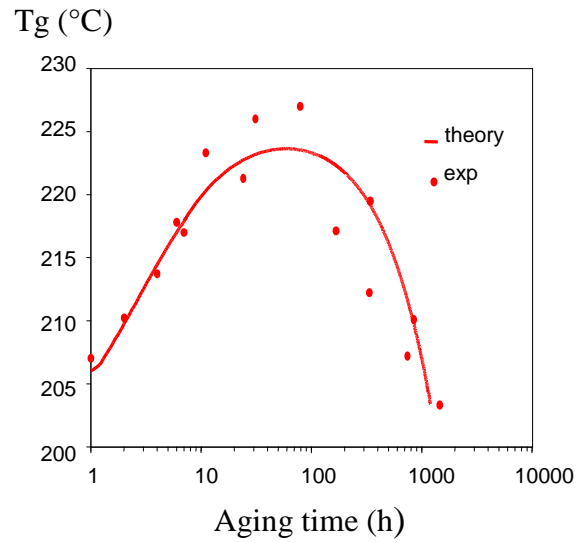

Fig.6. Evolution of the glass transition temperature after thermal aging at 210°C of an IMS carbon/977-2 epoxy composite [17].

4. Conclusion

In summary, to represent real use conditions of structural composites used for SST applications, it would be necessary to take into account all effects of aging factors and mechanical loading. Subsequently, modeling would become very complex. However, it was interesting to analyze the principal aging factors such as temperature and oxidizing atmosphere in conjunction with the mechanical data. Thermal aging introduces some degradation by physico-chemical

mechanisms arising homogeneously in the composite matrix.

The surface of materials is concerned with thermo-oxidation leading to molecular chain breaks at the atomic scale and to microcracks at the ply scale. These events participate to the decline in failure properties determined on QI composites aged under different conditions. Thermo-oxidation can be modeled by kinetics related to radical decomposition supplied by oxygen diffusion in the composite matrix. This model describes fairly well the thickness of the oxidized layer.

The bulk of the composite is concerned with some different aging manifestations such as thermolysis, phase separations, internal stress states, fiber/resin interface weakening. Thermolysis is an important parameter since it causes numerous changes within the chemical structure of the matrix. After thermal aging, the load transfer from fiber to the matrix can be modified but rather large change in matrix viscoelastic behavior while microcrack initiation and propagation also modify strength properties as a reduction.The glass transition temperature is in some kind representative for the health of the network. Knowing that a multiscale approach can be used for assessment the viscoelastic behavior of polymer matrix composites [19], Tg can constitute an internal variable to be integrated into this model. Results of creep behavior carried out on composites aged under various conditions are shown in the reference [20].

The investigation on both damage and mechanical data shows that aging of organic matrix composites is a matter very complex involving a lot of factors. To predict properties and behavior at use temperatures on the long-term, it would be necessary to develop a general physico-thermo-mechanical model. The task is difficult but with simplified assumptions, it seems that this proposal is starting gradually to take form.

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