A study of the mechanical behavior of thermo-oxidized composite lamina

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Abstract - The aim of this work is the study of the mechanical behavior of polymer matrix composites reinforced with carbon fiber, which have undergone a thermo-oxidation process. The purpose of this work is the multi-scale analysis of the consequences of oxidation of epoxy matrices on the intrinsic mechanical properties of the external composite ply, on the one hand, and on the internal mechanical states experienced by the structure as a function of the considered mechanical load, on the other hand. Effective mechanical properties of oxidized composite plies are determined according to Eshelby-Kröner self-consistent homogenization procedure, depending on the progress of the oxidation process. The results are compared to the corresponding properties estimated by the finite element method. The macroscopic mechanical states are calculated for T300/5208 unidirectional composite and laminates. The macroscopic stresses undergone by each ply of the structure was deduced from the classical lamination theory and by the finite element method, whereas the local stresses in both constituents (carbon fiber and epoxy matrix) were calculated for each ply of structure, through an analytical stress concentration relation previously demonstrated in [1], which satisfies the mathematical framework of Eshelby-Kröner self-consistent model. The local stresses have also been compared with the results obtained using the finite element method: the two approaches predict close together results.

Résumé - L’objectif de ce travail est l’étude du comportement mécanique des composites à matrice polymère renforcée avec la fibre de carbone, qui ont subi un processus de thermo-oxydation. Le but de ce travail est l’analyse multi-échelle des conséquences de l’oxydation de la matrice époxy sur les propriétés mécaniques intrinsèques de la couche extérieure en composite, d’une part, et sur la mécanique interne des états, par la structure en fonction de la charge mécanique considéré, d’autre part. Les propriétés mécaniques effectives du composite oxydé plies sont déterminées en fonction de la procédure d’homogénéisation de Eshelby-Kröner auto-cohérent, et en fonction de l’avancement du processus d’oxydation. Les résultats sont comparés aux propriétés correspondantes estimées par la méthode des éléments finis. Les mécaniques macroscopiques sont calculées pour les états T300/5208 composites unidirectionnels et stratifiés. Le stress subi par macroscopique de chaque pli de la structure a été déduite de la théorie classique de laminage et par la méthode des éléments finis, alors que comme il le souligne à la fois, les constituants (fibre de carbone et de résine époxy matrice) ont été calculées pour chaque pli de la structure, par le biais d’une analyse du stress concentration, relation déjà démontrée dans [1], qui répond aux mathématiques qu’au modèle auto-cohérent de Eshelby-Kröner modèle auto-cohérent. Les stress locaux ont également été comparés avec les résultats obtenus en utilisant la méthode des éléments finis: les deux approches prédissent des résultats proches.

Keywords: Thermo-oxidation - Polymer matrix composites - Scale transition models - Local stress.

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1. INTRODUCTION

Due to their very interesting specific mechanical properties, carbon-reinforced 
epoxy laminates are considered as serious candidates for the replacement of metals, 
metallic alloys and cermets for industrial applications such as structural parts for the 
next generation supersonic aircrafts [2].

The lifetime scheduled for the structural elements of supersonic aircraft 
approximately corresponds to 20,000 cycles in a range of temperatures varying between 
–55 °C and 120 °C, with a total length of the plateau at 120 °C of 80,000 h (10 years) [3].

Such high temperatures over long periods cause a thermal ageing of the resin of 
elements composite of structure leading to thermal oxidation of external ply of material. 
Before 1990, few studies have been conducted on thermal aging of organic matrix 
composites reinforced with carbon fiber.

Indeed, before this date, the use of these materials has been limited to a field of 
rather low temperatures between -50 °C and +70 °C, which correspond to the thermal 
load experienced in service by structural parts of, for example, subsonic aircraft and 
helicopters. Recently, the problem arose when such organic matrix composites have 
been considered for applications under severe environmental conditions from a thermal 
point of view (temperatures of about 250 °C, air pressure higher than 1 atmosphere) [4, 
5].

The laminated composites exposed to high temperatures are subject to degradation 
caused mainly by thermal oxidation of their organic matrix. It induces the growth of 
oxidized layer of reduced thickness in the subsurface of the composite parts. This 
superficial phenomenon leads to weight loss and alters the mechanical behavior [6, 7].

The diffusion-reaction model coupled to a mechanistic scheme has been proposed in 
[8], in order to predict the behaviour of epoxy matrices experiencing thermal ageing. It 
can predict the oxidation products concentration profiles, from which the oxidized layer 
thickness and weight losses are determined. The thermal oxidation of matrix induces a 
fragility of the near surface area from which the mechanical properties are different to 
those of the bulk, unaffected by oxidation material.

The purpose of this work is the multi-scale analysis of the consequences of the 
thermal-oxidation of epoxy matrices on the intrinsic mechanical properties of the 
external composite ply, on the one hand, and on the internal mechanical states of 
composite structure according to the considered mechanical loading, on the other hand.

This work includes five sections. The first section is dedicated to the influence of 
thermal oxidation on the mechanical properties of composite ply.

The second section presents the Eshelby-Kröner self-consistent model: its 
constitutive laws are given for the estimation of effective thermal elastic properties of 
composite ply (stiffness tensor and coefficient of thermal expansion).

The third section is devoted to the coupling of the classical lamination theory and 
analytical scale-transition relations for local stress determination in both constituents of 
composite plies subjected to a thermo-elastic loading.

The fourth section describes the conclusions of the present study, while the fifth 
offers a number of perspectives for future developments in this field of research.
2. EFFECTIVE PROPERTIES OF A THERMOOXIDIZED COMPOSITE PLY

Oxidation model and results

Various models enabling to achieve the numerical computation of oxidation process in pure epoxies or epoxy matrix composites have been proposed in the literature [9, 10]. Simulations of isothermal aging at 150 °C of an epoxy resin during various ageing lengths demonstrated that the oxidized layer thickness was not growing beyond 200 µm whereas the oxidation products concentration were continuously increasing in the affected layer [8].

Results obtained through ultra-micro indentation tests on epoxy resin, after 100 h, 600 h and 1000 h of isothermal aging at 150 °C show that a polynomial relation between elastic indentation modulus and oxidation products concentration occurs "(1)" [8]:

$$Y^m = -57.4Q^2 + 592Q + 4045$$  \hspace{1cm} (1)

where $Y^m$ is the elastic modulus of the epoxy matrix, expressed in GPa, $Q$ is the oxidation products concentration (mol/l) which is space and time dependent. The evolution of the Young’s modulus of the matrix during the thermal oxidation process is displayed on figure 1. The matrix is considered as an isotropic material, which Poisson’s ratio $\nu^m = 0.35$ is assumed due to the lack of available information on its evolution, as independent of state of thermal oxidation process, while its shear modulus is deducted from the classical relation:

$$G^m = \frac{Y^m}{2(1 + \nu^m)}$$  \hspace{1cm} (2)

Fig. 1: Evolution of the elastic modulus as a function of the oxidation products concentration

Comparison with the behavior of unaffected matrix

The thermal oxidized matrix is stiffer than the unaffected matrix in a ratio varying between 1 and 1.38. The matrix properties of a thermally oxidized ply can be very different from those of the corresponding unaffected ply, so that three main consequences due to the thermal oxidation of composite structure can be expected: a
variation of i- the effective macroscopic properties of composite plies, ii- the profiles of macroscopic stress in the structure and iii- the localization of the macroscopic mechanical states (stress and strain) in both constituents of each ply (fiber and matrix).

The three above listed expected consequences of thermo-oxidation are multi scale phenomena, either explicitly, in the case of items i- and iii-, (i- being an homogenization problem, whereas iii- is related to localization problem), or implicitly, in the case of item ii-, which implies the knowledge of the macroscopic effective properties of the composite ply (resulting from the estimates achieved in i-).

In order to be able to treat each of these aspects, a scale-transition model is required. This model is described below in section 3.

3. MULTI-SCALE ANALYSIS

3.1 Introduction

Scale transition models are based on a multiscale representation of materials. In the case of composite materials, for instance, a two-scale model is sufficient:

- The properties and mechanical states of either the resin or its reinforcements are respectively indicated by the superscripts \( m \) and \( f \). These constituents define the so-called ‘pseudo macroscopic’ scale of the material [11].

- Homogenization operations performed over its aforementioned constituents are assumed to provide the effective behavior of the composite ply, which defines the macroscopic scale of the model. It is denoted by the superscript \( ^I \). This definition also enables to consider an uni-directional reinforcement at macroscopic scale, which is a satisfactorily realistic statement, compared to the present design of composite structures.

As for the composite structure, it is actually constituted by an assembly of the above described composite plies, each of them possibly having the principal axis of their reinforcements differently oriented from one to another. This approach enables to treat the case of multi-directional laminates, as shown, for example, in [1].

Within scale transition modeling, the local properties of the \( i \)-superscripted constituents are usually considered to be known (i.e. the pseudo macroscopic stiffness, \( L_i \) and coefficients of thermal expansion \( M_i \)), whereas the corresponding effective macroscopic properties of the composite structure (respectively, \( L^I \) and \( M^I \)) are a priori unknown and results from (often numerical) computations.

Among the numerous, available in the literature scale transition models, able to handle such a problem, most involve rough-and-ready theoretical frameworks: Voigt [12], Reuss [13], Neerfeld-Hill [14, 15], Tsai-Hahn [16] and Mori-Tanaka [17, 18] approximates fall in this category.

This is not satisfying, since such a model does not properly depict the real physical conditions experienced in practice by the material. In spite of this lack of physical realism, some of the aforementioned models do nevertheless provide a numerically satisfying estimation of the effective properties of a composite ply, by comparison with the experimental values or others, more rigorous models.

Both Tsai-Hahn and Mori-Tanaka models fulfil this interesting condition [19, 20]. Nevertheless, in the field of scale transition modelling, the best candidate remains Kröner-Eshelby self-consistent model [21, 22], because only this model takes into account a rigorous treatment of the thermohygro-elastic interactions between the
homogeneous macroscopic medium and its heterogeneous constituents, as well as this model enables handling the microstructure (i.e. the particular morphology of the constituents, especially that of the reinforcements).

3.2 Determination of the effective macroscopic thermo-elastic properties of composite plies

According to Eshelby-Kröner self consistent model, the homogenization relation enabling to determine the macroscopic elastic stiffness of a composite ply from the properties of the constituents is:

$$L^I = \left( L^I : \left[ E^I : (L^I - L^I)^{-1} + I \right]^{-1} \right)_{i=f,m}$$  \hspace{1cm} (3)

In equation (3), $I$ stands for the fourth-order identity tensor, whereas the name given to the tensor $E^I$ often changes from one article to another (it is called, for example, Hill tensor, or Morris tensor, depending on which work from [28, 29] is considered). Morris’s tensor expresses the dependence of the localization tensor on the morphology assumed for the matrix and its reinforcements [28]. It can be expressed as a function of Eshelby tensor $S^I_{esh}$, through

$$E^I = S^I_{esh} : L^{-1}$$

It has to be underlined that both Hill’s and Eshelby’s tensor components are functions of the macroscopic stiffness $L^I$ (some examples are given in [23, 24]).

The homogenization relation satisfied by the macroscopic coefficients of thermal expansion of a composite ply writes as follows:

$$M^I = L^{I-1} : \left( [E^I : (L^I - L^I)^{-1} I]^{-1} : L^I : M^I \right)_{i=f,m}$$  \hspace{1cm} (4)

Only a few study studies were dedicated to the oxidation effects on the mechanical behavior of organic matrix composites. It was nevertheless shown in [25] that the properties of carbon fibers are stable below 300 °C.

As a consequence, the variation of mechanical properties of thermo-oxidized laminates only depend on the evolution of the matrix properties. Table 1 displays the local properties of carbon fiber considered in order to achieve the homogenization calculations.

| Table 1: Local properties of carbon fiber T300 [26] |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $Y_1$ (GPa)     | $Y_2$, $Y_3$ (GPa) | $\nu_{12}$, $\nu_{13}$ | $G_{12}$ (GPa) | $G_{23}$ (GPa) |
| 230             | 15              | 0.2             | 15              | 7               |

Evolutions of the effective longitudinal and transverse macroscopic elastic moduli, as a function of the oxidation products concentration are shows on figures 2 and 3, for a composite containing a carbon fiber volume fraction equal to 60 %. The effective mechanical properties of the oxidized composite ply were determined, during the oxidation process, through Eshelby-Kröner self-consistent homogenization procedure ‘(3)’ (curve ‘KESC’). The results were compared to the corresponding properties estimated according to the finite element method (FEM "curve").
Figure 2 shows the longitudinal macroscopic effective elastic modulus of a composite ply, as a function of the oxidation products concentration.

Figure 3 shows the transverse macroscopic effective elastic modulus of a composite ply, as a function of the oxidation products concentration.

Figure 4 shows the evolutions obtained for the effective macroscopic coefficients of thermal expansion of a composite ply, according to ‘(4)’, during the thermal oxidation process experienced by the epoxy.

Figure 4: Evolution of the longitudinal (\(M_{11}\)) and transverse (\(M_{22}\)) macroscopic coefficients of thermal expansion, as a function of the oxidation products concentration.
According to figure 2 and 4, the longitudinal effective properties (i.e. in the direction parallel to axis of the reinforcing fibers), are, in first approximation, independent from the state of thermal oxidation process of the polymer matrix constituting the considered composite ply.

Actually, a relative deviation weaker than 1 % is observed at the end of the oxidation process for the Young’s modulus, while the longitudinal macroscopic coefficient of thermal expansion remains almost constant (and tends towards zero). This result is explained by the fact that in the fiber direction, a unidirectional ply presents thermo-mechanical properties which are controlled by the properties of a single constituent: the fiber.

Experimental results on composite plies in similar circumstances, i.e. in cases when the carbon fibers exhibit constant properties, while those of the matrix significantly vary, corroborates the results of our simulations: longitudinal effective macroscopic properties of composite plies do not vary as a function of the properties polymer matrix (at least in the case that the composite ply contains a high volume fraction of fibers) [27]. On the contrary, the effective macroscopic properties of a composite ply, in the direction transverse to the reinforcements axis, do significantly depend on the state of thermal oxidation process experienced by the polymer matrix constituting the ply.

In fact, the relative variation of transverse Young modulus of oxidized ply compared to the reference value (unaffected ply) can reach 12 % at the term of oxidation process (and spreads so that the variation for transversal coefficient of thermal expansion is 3.5%). The reader will notice that this relative variation depends him even on the volume fraction of reinforcements in the composite ply and may reach 38 % in the pure matrix at the end of the oxidation process.

4. STUDY OF THE MULTI-SCALE MECHANICAL STATES EXPERIENCED BY THE COMPOSITE STRUCTURE

Determination of mechanical states within the constituents of a composite ply subjected to thermo-elastic loading

Analytical relations satisfying the fundamental assumptions of Eshelby-Kröner self-consistent model, enabling to proceed to the localization of the macroscopic strains within the matrix were established in [1].

Due to the length of these equations, they will not be provided in the present work, so that the interested reader should refer to ‘(18)’-‘(19)’ of [1]. The corresponding stress tensor experienced by the matrix can be deduced from its strain state through:

\[
\sigma^m = \begin{bmatrix}
\sigma^m_{11} & 2^m_{14} \varepsilon^m_{12} & 2^m_{14} \varepsilon^m_{13} \\
2^m_{14} \varepsilon^m_{12} & \sigma^m_{22} & 2^m_{14} \varepsilon^m_{23} \\
2^m_{14} \varepsilon^m_{13} & 2^m_{14} \varepsilon^m_{23} & \sigma^m_{33}
\end{bmatrix}\]

(5)

With

\[
\begin{align*}
\sigma^m_{11} &= L^m_{11} \varepsilon^m_{11} + L^m_{12} (\varepsilon^m_{22} + \varepsilon^m_{33}) - M^m_{11} (L^m_{11} + 2^m_{12}) \Delta T \\
\sigma^m_{22} &= L^m_{11} \varepsilon^m_{22} + L^m_{12} (\varepsilon^m_{11} + \varepsilon^m_{33}) - M^m_{11} (L^m_{11} + 2^m_{12}) \Delta T \\
\sigma^m_{33} &= L^m_{11} \varepsilon^m_{33} + L^m_{12} (\varepsilon^m_{11} + \varepsilon^m_{22}) - M^m_{11} (L^m_{11} + 2^m_{12}) \Delta T
\end{align*}
\]

(6)
The mechanical states experienced by the reinforcements can be deduced from Hill’s averages relations over stresses and strains [28]:

$$\sigma^f = \frac{1}{\nu^f} \sigma^I - \frac{\nu^m}{\nu^f} \sigma^m ; \quad \varepsilon^f = \frac{1}{\nu^f} \varepsilon^I - \frac{\nu^m}{\nu^f} \varepsilon^m$$

(7)

The variation of the internal macroscopic stresses $\sigma^I_{11}$ and $\sigma^I_{22}$ have been calculated during the one edge thermal oxidation process of a composite laminate submitted to either a longitudinal or a transverse external load. The results obtained for the macroscopic mechanical states were localized within the constituents using the above described scale transition relations.

The curves for both the macroscopic and local stresses experienced by the external ply have been displayed on figures 5-6 (in the cases that a longitudinal or a transverse external load was considered, respectively). On the same figures, the stress states predicted for the thermo-oxidized laminate were compared to the corresponding stresses calculated for the unaffected material.

The mechanical states predicted from the effective macroscopic properties provided by Eshelby-Kröner Self-Consistent model were compared to the mechanical states calculated from the effective macroscopic properties deduced from finite elements analysis.

Figures 5 and 6 underline the consequences of a thermal oxidation on the multi-scale mechanical states. In the case that the composite structure is submitted to a longitudinal external load, the multi-scale internal stresses experienced by the oxidized ply are independent from the oxidation process state.

This result comes from the independence from the oxidation state exhibited by the macroscopic effective properties in the longitudinal direction (see section 4 of the present work).

On the contrary, in the case when the composite plate is submitted to a transverse mechanical loading, the internal stresses experienced by the oxidized ply and its very constituents differ from those that would have been undergone by an unaffected ply; the macroscopic stress increases during the thermal oxidation, as a consequence of the increased effective stiffness of the thermo-oxidized ply.
At the scale of the constituents:

i) the stress concentration in the reinforcing fiber does not vary at all as a function of the oxidation products concentration, since the properties of the carbon fibers are unchanged during the thermal-oxidation process.

ii) the epoxy matrix experiences an increasing stress state during the thermal oxidation process, which can be attributed to the increased stiffness of this constituent induced by the thermal-oxidation. Actually, composites are generally designed so that the reinforcements concentrate the stresses.

Moreover, in practice, damage and failure initially often takes place in the subsurface of a mechanical part. Thus, an increased stress experienced by the resin of the external ply is, a priori not favourable to the durability of the composite structure. These considerations can help to explain the worst durability of thermo-oxidized composite structures, observed in practice, by comparison with the reference behaviour of the unaffected by oxidation structure.
5. CONCLUSIONS

In this work, the consequences due to the thermal oxidation of the epoxy resin constituting a composite structure were investigated, for the first time, through a scale transition approach. The results obtained through the scale transition method were compared to finite elements calculations, with a rather good agreement. The scale transition approach demonstrates that the effective properties and mechanical states of the external ply of a composite structure having experienced a thermal oxidation process do not strongly differ from the corresponding reference values of the ply unaffected by the thermal oxidation.

On the opposite, the local properties and mechanical states of the matrix constituting the ply affected by thermal oxidation do strongly vary as a function of the thermal oxidation process state. It was demonstrated that both the evolutions of the mechanical properties and mechanical states in the epoxy after the thermal oxidation were not compatible with an enhanced durability of the structure, especially in the case that a transverse external load had to be undergone.

6. PERSPECTIVES

The scope of the present study was limited to the consequences of the thermal oxidation of the polymer matrix on the evolutions of the properties and mechanical states of composite materials during a subsequent loading at ambient temperature.

Nevertheless, the composite experiencing thermal ageing are often subjected to thermal mechanical loads at high temperature. Under these conditions, the polymer matrix exhibits a visco-elastic behavior. This leads to an effective visco-elastic behavior of the composite plies at macroscopic scale. In order to take into account these physical phenomena, a visco-elastic scale transition model will be developed.

This model will be used in order to achieve the prediction of the effective thermo-mechanical behaviour (stiffness tensor and coefficients of thermal expansion) of the composite plies as a function of time and temperature. Thereafter, it will be possible to
proceed to the localization of the mechanical states within the constituents of each ply of the studied composite structure.

Moreover, practical studies, published in the literature, report an evolution of the yield strength of epoxies during the thermal oxidation process. Multi-scale failure criteria, enabling to take into account these experimental results will be developed in further works, in order to rigorously investigate the durability of structures having been submitted to thermal oxidation processes.

REFERENCES


