

A multi-scale analysis of the mechanical behavior of thermo-oxidized C/epoxy lamina

A. Yousfi¹, S. Fréour^{2*}, F. Jacquemin², M. Rahmani¹, H. Osmani³, R. Guillén²

¹ Department of Mechanical Engineering, University of Laghouat, Algeria.

² GeM – Institut de Recherche en Génie Civil et Mécanique, UMR CNRS 6183, Université de Nantes - Ecole Centrale de Nantes, France.

³ Nonmetallic Materials Laboratory, University of Setif, Algeria.

* Corresponding author: sylvain.freour@univ-nantes.fr

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 matrix cracking is partly induced by the epoxy-resin oxidation, which involves a weight loss and a density increase, and as a consequence, shrinkage of the skin layer [1]. The oxidation induces some matrix shrinkage which generates high local stresses [2]. The purpose of this work is the multi-scale analysis of the consequences of oxidation and shrinkage 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 [3], 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.

Keywords: thermo-oxidation, polymer matrix composites, scale transition models, local stresses.

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 [4]. 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 (20 years) [5]. Such high temperatures over long periods cause a thermal ageing of the constitutive resin of composite elements of the structure. Before 1990, few studies have been conducted on thermal ageing 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 $+70^{\circ}\text{C}$, which correspond to the thermal load experienced in service by structural parts of, for example, subsonic aircraft and helicopters. Nevertheless, some important pioneering work have been achieved [6, 7, 8]. Recently, the problem arose when such organic matrix

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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) [9, 10]. It is now well established that, when they are exposed to high temperatures in air, organic matrix composites perish by thermal oxidation of the matrix [6, 11]. A key feature of this ageing process is that degradation is non uniform in the sample thickness because oxidation is diffusion controlled. In the last 20 years, many attempts were made to model these degradation gradients and thus, to obtain a realistic description of organic matrix thermal ageing. Some authors have contributed to this research by derivating, from a radical chain oxidation mechanism, a kinetic model coupling oxygen reaction and diffusion [12].

This model predicts, at every time t , for every elementary thickness layer located at the depth x beneath the sample surface, various physicochemical quantities among which: weight and density variations [12]. The knowledge of both quantities enables to determine the volume change (oxidation induces "hindered" shrinkage in thick parts), which is expected to generate a stress state responsible for the cracking of the external plies [13] of a composite structure. But, this volume change can be predicted only if the local mechanical properties are known. More recently, it was shown that a second important consequence of thermal ageing in epoxy networks is the decrease of the glass transition temperature (T_g), linked to predominant chain scission, and the increase of the glassy modulus at ambient temperature, attributed to an internal anti-plasticization effect [14]. Non empirical relationships linking the local structural state of epoxy network to the resulting glassy modulus are in course of elaboration yet [14]. Fortunately, empirical relationships have been proposed [15-16] and will be considered, in a first approach, here.

The purpose of this work is the multi-scale analysis of the consequences of the thermal-oxidation and the shrinkage 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.

1. Effective properties of a thermo-oxidized composite ply

1.1 Oxidation model and results:

Various model enabling to achieve the numerical computation of oxidation process in pure epoxies or epoxy matrix composites have been proposed in the literature [16, 17]. Simulations of isothermal aging at 150°C of an epoxy resin during various ageing duration demonstrated that the oxidized layer thickness was not growing beyond 200 μm whereas the oxidation products concentration were continuously increasing in the affected layer [18]. The averaged depth values of matrix shrinkage measured on specimens maintained 400 and 600 h at 150 °C in air are close ($\sim 1.5 \mu\text{m}$) but quite lower than those measured on samples submitted to 500 thermal cycles (2.2 μm) [19]. Results obtained through ultra-micro indentation tests on epoxy resin, after 100h, 600h and 1000h of isothermal aging at 150°C show that an empirical relationship between elastic indentation modulus and oxidation products concentration occurs (Eq. 1) [18]:

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$$Y^m = 5479 - 1460 \times \text{Exp}(-0.79 Q) \quad (1)$$

where Y^m is the elastic modulus of the epoxy matrix, expressed in MPa, Q is the oxidation products concentration (mol/L) which is space and time dependent. Obviously, the elastic modulus $Y_0^m = 4019$ MPa is obtained through (1), in the case that the condition $Q = 0$ mol/L is taken into account. It must be underlined here, that this relationship (1) is not rigorously based on theoretical concepts. It was obtained by fitting a combination of experimental and theoretical results. It is only valid for the temperature under consideration (150°C). It would be surprising that this relationship was also valid for other thermal ageing conditions. Consequently, the predictions made in this publication are tributary to this relationship. 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 deduced from the classical relation:

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

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 2.

2. Multi-scale Analysis

2.1 Introduction:

Scale transition models are based on a multi-scale 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 [20].
- Homogenisation operations performed over its aforementioned constituents are assumed to provide the effective behaviour of the composite ply, which defines the macroscopic scale of the model. It is denoted by the superscript ^l. This definition also enables to consider an unidirectional reinforcement at macroscopic scale, which is a satisfactorily realistic statement, compared to the present design of composite structures.

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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 [3]. Within scale transition modeling, the local properties of the i -superscripted constituents are usually considered to be known (i.e. the pseudo-macroscopic stiffnesses, \mathbf{L}^i and coefficients of thermal expansion \mathbf{M}^i), whereas the corresponding effective macroscopic properties of the composite structure (respectively, \mathbf{L}^I and \mathbf{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 [21], Reuss, [22], Neerfeld-Hill [23-24] Tsai-Hahn [25] and Mori-Tanaka [26, 27] 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 [28, 29]. Nevertheless, in the field of scale transition modelling, the best candidate remains Kröner-Eshelby self-consistent model [30, 31], because only this model takes into account a rigorous treatment of the thermo-hygro-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).

It should be underlined, also, that the above cited models assume that at the smallest considered scale (the base volume of the heterogeneities, i.e. the pseudo-macroscopic scale, in the present work), the properties are uniform. This means that, in order to achieve the simulations, it will be necessary to assume that the matrix of the surface ply has uniform properties through its thickness, which does not correspond to the true evolution described in the literature [18].

2.2 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:

$$\mathbf{L}^I = \left\langle \mathbf{L}^i : \left[\mathbf{E}^I : (\mathbf{L}^i - \mathbf{L}^I) + \mathbf{I} \right]^{-1} \right\rangle_{i=f,m} \quad (3)$$

In equation (3), \mathbf{I} stands for the fourth-order identity tensor, whereas the name given to the tensor \mathbf{E}^I often changes from one article to another (it is called, for example, Hill tensor, or Morris tensor, depending on which work from [32-33] is considered). Morris's tensor expresses the dependence of the localization tensor on the morphology assumed for the matrix and its reinforcements [32]. It can

be expressed as a function of Eshelby tensor \mathbf{S}_{esh}^I , through $\mathbf{E}^I = \mathbf{S}_{esh}^I : \mathbf{L}^{I^{-1}}$.

It has to be underlined that both Hill's and Eshelby's tensor components are functions of the macroscopic stiffness \mathbf{L}^I (some examples are given in [34, 35]).

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

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$$\mathbf{M}^I = \mathbf{L}^{I^{-1}} : \left\langle \left[\mathbf{E}^I : (\mathbf{L}^i - \mathbf{L}^I) + \mathbf{I} \right]^{-1} : \mathbf{L}^i : \mathbf{M}^i \right\rangle_{i=f,m} \quad (4)$$

Only few studies were dedicated to the oxidation effects on the mechanical behavior of organic matrix composites [16, 36-37]. It was nevertheless shown in [38] 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.

Evolutions of the effective longitudinal and transverse macroscopic elastic moduli, as a function of the oxidation products concentration are shown 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 (Eq. 3) (curve "KESC"). The results were compared to the corresponding properties estimated according to the finite element method (FEM "curve").

Figure 4 shows the evolutions obtained for the effective macroscopic coefficients of thermal expansion of a composite ply, according to equation (4), during the thermal oxidation process experienced by the epoxy. In order to achieve the computations, the following pseudo-macroscopic coefficients of thermal expansion were considered: $M_{11}^m = M_{22}^m = M_{33}^m = 60.10^{-6} \text{ K}^{-1}$, $M_{11}^f = -0.7 \cdot 10^{-6} \text{ K}^{-1}$, $M_{22}^f = M_{33}^f = 12.10^{-6} \text{ K}^{-1}$. Since the literature does not report the evolution of the CME during the oxidation process of the matrix, the pseudo-macroscopic CME considered in the present work are obviously those of the unaffected constituents, as published in [39].

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) [40]. 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 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.

3 Study of the multi-scale mechanical states experienced by the composite structure

3.1 Matrix shrinkage effect on the mechanical states of the thermo-oxidized composite

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The oxidation of the epoxy matrix results in a loss of mass and a reduction in volume of the matrix, inducing shrinkage of the this constituent with respect to the fibres [41]. 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 to crack initiation [42]. The total strain in matrix $\boldsymbol{\varepsilon}_T^m$ is:

$$\boldsymbol{\varepsilon}_T^m = \boldsymbol{\varepsilon}_E^m + \boldsymbol{\varepsilon}_S^m \quad (5)$$

Where $\boldsymbol{\varepsilon}_E^m$ is the elastic strain of matrix, whereas $\boldsymbol{\varepsilon}_S^m$ which denotes the strain due to the shrinkage of matrix, depends on its oxidation state.

$$\boldsymbol{\varepsilon}_S^m = \begin{bmatrix} \delta_{11}^m & 0 & 0 \\ 0 & \delta_{11}^m & 0 \\ 0 & 0 & \delta_{11}^m \end{bmatrix} Q \quad (6)$$

where $\delta_{11}^m = \frac{\varepsilon_S(Q_{\max})}{Q_{\max}}$, and $\varepsilon_S(Q_{\max}) = 2,5\%$ the maximal strain due to the matrix shrinkage [43].

3.2 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 [3], in the case that the material was subjected to a hygroelastic load. Due to the length of these equations, they will not be provided in the present work, so that the interested reader should refer to equations (19-20) of [3]. In these equations, $\boldsymbol{\beta}$ stands for the coefficients of moisture expansion, whereas ΔC is the moisture content, which, contrary to the temperature, is generally considered, for the purpose of the scale transition modelling, as heterogeneous in a given ply, so that $\Delta C^I \neq \Delta C^m \neq \Delta C^f$. Introducing in these equations the replacement rules $\beta_{11}^m \rightarrow M_{11}^m$, $\beta_{11}^r \rightarrow M_{11}^r$, $\beta_{22}^r \rightarrow M_{22}^r$, $\beta_{11}^I \rightarrow M_{11}^I$, $\beta_{22}^I \rightarrow M_{22}^I$, $\Delta C^I \rightarrow \Delta T^I$, $\Delta C^m \rightarrow \Delta T^m$, and taking into account the case of a uniform distribution of the temperature within the constituents of the ply (i.e. $\Delta T^I = \Delta T^m = \Delta T^f$) yields the following analytical relation for the localization of the macroscopic strains in the matrix of a uni-directionally fiber-reinforced ply:

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$$\left\{ \begin{array}{l} \varepsilon_{11}^m = \varepsilon_{11}^I \\ \varepsilon_{12}^m = \frac{2 L_{55}^I \varepsilon_{12}^I}{L_{55}^I + L_{44}^m} \\ \varepsilon_{13}^m = \frac{2 L_{55}^I \varepsilon_{13}^I}{L_{55}^I + L_{44}^m} \\ \varepsilon_{22}^m = \frac{N_1^m + N_2^m + N_3^m + N_4^m}{D_1^m} \\ \varepsilon_{23}^m = \frac{2 L_{22}^I (L_{22}^I - L_{23}^I) \varepsilon_{23}^I}{2 L_{22}^I + L_{23}^I (L_{44}^I - L_{44}^m) + L_{22}^I (3 L_{44}^m - 2 L_{23}^I - 3 L_{44}^I)} \\ \varepsilon_{33}^m = \varepsilon_{22}^m - 4 L_{22}^I \frac{(L_{22}^I - L_{23}^I) (\varepsilon_{22}^I - \varepsilon_{33}^I)}{L_{22}^I + 3 L_{22}^I (L_{11}^m - L_{12}^m) - L_{23}^I (L_{11}^m + L_{23}^I - L_{12}^m)} \end{array} \right. \quad (7)$$

where,

$$\left\{ \begin{array}{l} N_1^m = M_{11}^m (L_{11}^m + 2 L_{12}^m) \Delta T - (M_{11}^I L_{12}^I + M_{22}^I (L_{22}^I + L_{23}^I)) \Delta T \\ N_2^m = (L_{12}^I + L_{12}^m) \varepsilon_{11}^I \\ N_3^m = \frac{L_{22}^I \left\{ L_{22}^I (5 L_{11}^m - L_{12}^m + 3 L_{22}^I) - L_{23}^I (3 L_{11}^m + L_{12}^m + 4 L_{22}^I) + L_{23}^I \right\}}{(3 L_{22}^I - L_{23}^I) (L_{11}^m - L_{12}^m) + L_{22}^I - L_{23}^I} \varepsilon_{22}^I \\ N_4^m = \frac{L_{22}^I \left\{ L_{22}^I (L_{11}^m - 5 L_{12}^m + L_{22}^I) - L_{23}^I (L_{11}^m + 3 L_{12}^m + 4 L_{22}^I) + 3 L_{23}^I \right\}}{(3 L_{22}^I - L_{23}^I) (L_{11}^m - L_{12}^m) + L_{22}^I - L_{23}^I} \varepsilon_{33}^I \\ D_1^m = L_{11}^m + L_{12}^m + L_{22}^I - L_{23}^I \end{array} \right. \quad (8)$$

The corresponding stress tensor experienced by the matrix can be deduced from its strain state through:

$$\sigma^m = \begin{bmatrix} \sigma_{11}^m & 2 L_{44}^m \varepsilon_{12}^m & 2 L_{44}^m \varepsilon_{13}^m \\ 2 L_{44}^m \varepsilon_{12}^m & \sigma_{22}^m & 2 L_{44}^m \varepsilon_{23}^m \\ 2 L_{44}^m \varepsilon_{13}^m & 2 L_{44}^m \varepsilon_{23}^m & \sigma_{33}^m \end{bmatrix} \quad (9)$$

with:

$$\left\{ \begin{array}{l} \sigma_{11}^m = L_{11}^m \varepsilon_{11}^m + L_{12}^m (\varepsilon_{22}^m + \varepsilon_{33}^m) - M_{11}^m (L_{11}^m + 2 L_{12}^m) \Delta T \\ \sigma_{22}^m = L_{11}^m \varepsilon_{22}^m + L_{12}^m (\varepsilon_{11}^m + \varepsilon_{33}^m) - M_{11}^m (L_{11}^m + 2 L_{12}^m) \Delta T \\ \sigma_{33}^m = L_{11}^m \varepsilon_{33}^m + L_{12}^m (\varepsilon_{11}^m + \varepsilon_{22}^m) - M_{11}^m (L_{11}^m + 2 L_{12}^m) \Delta T \end{array} \right. \quad (10)$$

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The mechanical states experienced by the reinforcements can be deduced from Hill's averages relations over stresses and strains [32]:

$$\sigma^f = \frac{1}{v^f} \sigma^I - \frac{v^m}{v^f} \sigma^m; \quad \varepsilon^f = \frac{1}{v^f} \varepsilon^I - \frac{v^m}{v^f} \varepsilon^m \quad (11)$$

In the present study, the case of a thin laminated (0°-0°) plate (thickness 1600 μm) constituted of 8 plies, as shown on figure 5, was considered for achieving the computations. The oxidation process is assumed to occur only from one edge, and to affect only the first (external) ply.

The variations of the internal macroscopic stresses σ_{11}^I and σ_{22}^I have been calculated during the one edge thermal oxidation process of the composite laminate submitted to either external loads (the structure experiencing either a pure longitudinal load $\sigma_{11} = 100$ MPa, a pure transverse load $\sigma_{22} = 50$ MPa, or a pure shear stress $\sigma_{12} = 25$ MPa). A similar study was achieved on an unidirectionally reinforced plate experiencing a pure thermal loading corresponding to a temperature increment $\Delta T = 100^\circ\text{C}$. 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 6 to 9 (in the cases that a longitudinal, a transverse, a shear external load or a thermal 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 (achieved using Matlab software).

Figures 6 to 9 underline the consequences, predicted by the present approach, of a thermal oxidation on the multi-scale mechanical states in the oxidized ply and its first neighbour, which is considered to remain unaffected, according to the literature [18].

- i) 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 can be attributed to the independence from the oxidation state exhibited by the macroscopic effective properties in the longitudinal direction (see section 3 of the present work).
- ii) An oxidation free unidirectionally reinforced composite structure submitted to an uniform thermal load does not experience stress at ply scale. A very similar situation occur in the case that a pure thermal load is applied to a partially (i.e. partially versus the depth) oxidized structure. A weak stress level occur in the first and second plies of the oxidized structure, due to their heterogeneous thermo-mechanical properties. This result comes from the relatively weak evolution predicted by the present approach for the macroscopic effective coefficients of thermal expansion as a function of the oxidation products concentration (according to figure 4). Nevertheless, it should be underlined that the data used in the present study in order to account for the consequences of thermal oxidation and matrix shrinkage over the effective properties of composite plies do not involve pseudo-macroscopic CTE (especially those of the epoxy) which depend themselves on the oxidation state, due to lack of available published experimental results. As a consequence, the numerical simulations, which results were displayed on figure 9 should be considered carefully, as a preliminary study only, the conclusions of which could be revised as the

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true pseudomacroscopic thermo-mechanical properties of thermo-oxidized epoxies would have been more extensively investigated in the literature. Moreover, one of the most significant factor in the thermo-oxidation of resins: the shrinkage due to off gassing of oxidation by-products is accounted for in the present manuscript. Actually, the shrinkage is eventually manifested as ply cracks due to the development of oxidation induced residual stress. These effects are not negligible compared to residual stresses due to CTE mismatches between the plies.

- iii) On the contrary, in the case when the composite plate is submitted to a transverse mechanical loading, or an in-plane shear stress (see figures 7, 8) 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.
- iv) At the scale of the constituents, the stress concentration in the reinforcing fiber does not vary, in first approximation, as a function of the oxidation products concentration, since the properties of the carbon fibers are unchanged during the thermal-oxidation process.
- v) On the second hand, 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.
- vi) In any case, the significant effects induced by a thermal oxidation process on the multi-scale mechanical states experienced by a thin composite plate are almost limited to the oxidized ply itself. Actually, the first unaffected ply neighbouring the oxidized ply does not experience a significant evolution of its mechanical states at any scale, as a function of the oxidation state of the oxidized ply.

4 Conclusions

In this work, the consequences due to the thermal oxidation and the shrinkage of the epoxy resin constituting a composite structure were investigated, for the first time, through a scale transition approach. The obtained results 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 and the matrix shrinkage 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 or an in plane shear stress had to be undergone. Nevertheless, the present approach does not underline that the service life of a composite plate submitted to longitudinal or thermal load would be affected by the thermal oxidation of the epoxy.

5 Perspectives

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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 [43-44]. Furthermore, a significant factor in the oxidation of resins is shrinkage due to off gassing of oxidation byproducts [43]. The shrinkage is eventually manifested as ply cracks due to the development of oxidation induced residual stresses. 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.

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