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The employment of 0/90 unsymmetric samples for the characterisation of the thermo-oxidation behaviour of composite materials at high temperatures

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ABSTRACT

The present paper explores the possibility to employ 0/90 unsymmetric plates as a tool for characterising the thermo-oxidation behaviour and the environmental ageing of composite materials at high temperature. The continuous monitoring of the out of plane displacements and the curvatures of such samples can be used for the identification of the thermo-oxidation induced irreversible chemical strain/stress build up and material property changes. A model has been developed to take into account the effects of thermo-oxidation on the time-dependent plate curvatures. Simulations show that 0/90 unsymmetric plates are very sensitive to thermo-oxidation induced changes, thus effective for capturing the searched thermo-oxidation effects. The predictions of the present model may serve for parametric studies and design of tests.

1. Introduction

There is an abundant literature concerning the employment of 0/90 unsymmetric plates as an experimental tool for composite materials. So far such plates have been employed for the measurement, the simulation and the experimental characterisation of:

- residual thermal stress in composites cured by the autoclave technique, in which the main source of residual stress is the temperature differential related to the cooldown from cure temperature to room temperature [1–6],
- residual stress of hygrothermal nature, in which the stress development is due to moisture absorption of the polymer resin material [7–10],
- damage monitoring [11,12],
- smart composites, exploiting the multistable behaviour of such structures [13–16].

It is now widely understood that 0/90 unsymmetric plates (narrow strips or large square panels) are an effective tool to monitor internal stress of thermal nature arising in cured composites but also the transient behaviour of composites exposed to the environment. In fact, the real-time monitoring of the out of plane displacements and of the plate curvatures helps visualising in a quite simple manner any possible interaction of the composite material with its environment and any possible material evolution related to such interaction.

However, not much research concerning the long-term behaviour of such plates is available in the literature. Despite its unique features, the 0/90 unsymmetric plate sample has not been fully exploited in the transient and the long-term regime. Moreover all the studies concerned with the multistability behaviour of such panels and the exploitation of such behaviour for the realisation of smart structures have rarely touched the important question of how this multistable behaviour changes when the structure is exposed to the real environment for a long time.

This point is really crucial for the design of smart structures and needs to be addressed.

The present paper explores the possibility to employ 0/90 unsymmetric plates as a tool for characterising the thermo-oxidation behaviour and the environmental ageing of composite materials at high temperatures (>120 °C). The continuous monitoring of the out of plane displacements and the curvatures of such samples is used for the identification of the thermo-oxidation induced irreversible chemical strain/stress build up and material property changes.

Thermo-oxidation in composites and polymer composites has been widely studied in the literature (see, for instance, references [23–32]), a consistent amount of experimental and theoretical research has allowed identifying the main effects of thermo-oxidation in polymers and polymer composites. Thermo-oxidation consists in a coupled reaction–diffusion phenomenon which produces mass and density variations and irreversible residual strains ("shrinkage" strains) responsible for residual stress. Other effects consist in a substantial change (increase) of the local mechanical properties (Young's modulus, for instance) due to local "disruption" of the macromolecular chains and to the internal antiplastici-

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zation of the epoxy network ([28]), decrease of the local "resistance" of the materials and, possibly, embrittlement.

At the microscopic scale (the scale of a fibre) this behaviour may give rise to local shrinkage matrix strains/stresses which in turn may promote debonding at the fibre/matrix interface and accelerate the onset of damage. At the meso/macroscopic scale (the scale of a ply or a laminate) thermo-oxidation promotes mass loss but may be also responsible for onset and fast propagation of matrix cracks due to the embrittlement of the resin.

Previous research on polymers allowed identifying the thermo-oxidation chemical reaction–diffusion phenomenon [26,27], the thermo-oxidation induced matrix shrinkage [27,31] and mass loss [26,27], the local polymer material changes [29], composite mass loss and degradation [32].

The studies concerning the development of thermo-oxidation induced strains and stresses have been mainly carried out at the microscopic level, leading to the identification of local strain and stress states [31]: thermo-oxidation modifies the mechanical properties of the polymer and such modifications take place along a very thin material layer. When the composite is concerned, fibre–matrix interfaces may play a major role in the oxygen reaction/diffusion process and the development of thermo-oxidation induced matrix shrinkage may eventually lead to local fibre–matrix debonding. For a composite exposed to atmospheric air at 150 °C the apparition of fibre–matrix debonding is expected after around 1000 h [31].

It is essential to develop an experimental test/device for the characterisation of thermo-oxidation effects in composite materials.

We think that 0/90 plates are an attractive tool to this aim. In such structures, the thermo-oxidation induced change of the mechanical properties may promote changes of the measurable curvatures.

Many of the cited studies on 0/90 plates employ the classical lamination theory (CLT), which is a materially and geometrically linear theory, to predict the deformed shape of such plates. Hyer showed and explained first the multistable behaviour of 0/90 unsymmetric cured composite plates [17,18]. Depending on the in-plane dimensions, the temperature differential from the cure temperature and the thickness, the thickness ratio, e_0/e_{90} (the ratio between the 0° and 90° ply thickness), these plates may exhibit a unique saddle-like shape, which is stable at room temperature, or two cylindrical-like shapes, (along the longitudinal or the transverse direction, respectively) which are both stable at room temperature but separated by a snap-through event. Hyer developed also a quite simple model to predict the cured shapes of 0/90 unsymmetric plates [18]. This model is based on a four parameters Rayleigh–Ritz method and takes into account linear constitutive equations and geometrical nonlinearities (Von-Karman plate); its predictions for square plates are in excellent agreement with experiments and with more sophisticated finite elements models. Hyer's model has been widely discussed and further developed in the literature (see, for instance [19–22]) and it has been shown that its predictions may depend consistently on the in-plane dimensions of the plate. For instance ([21]) narrow strip samples (plates with high aspect ratio $AR = 10$) exhibit a quasi-saddle deformed shape along the whole range of temperatures and behave almost linearly, in accord with the CLT. This is an interesting result, since the experimenter may employ very narrow strips when he needs to avoid the complex multistability behaviour of large square plates and use the simple CLT. On the other hand one may be interested by the peculiar multistable behaviour of large square panels and exploit it for experimental purposes: for instance it has been shown in [10] that the multistability behaviour of large 0/90 plates can be conveniently used to separate the effects of thermal and hygroscopic fluctuations, to amplify the sensitivity of thermal and hygroscopic stress measures. Trespassing the bifurcation point during a transient hygroscopic conditioning may be useful for the effective monitoring of the whole moisture absorption process.

In this paper, among other, we will explore the effects of thermo-oxidation on the complex deformation behaviour of 0/90 composite plates. The paper is organised as follows: Section 2 presents the model approach, starting from the review of the mechanistic scheme for thermo-oxidation [26], the theoretical formulation of the irreversible chemical shrinkage strains [26,27] and the effects of thermo-oxidation on the ultra-micro indentation elastic (EIT) moduli [29]. The thermo-oxidation affected material properties of the composite are also presented starting from a simple homogenisation scheme. Finally, a model for simulating the deformation of 0/90 unsymmetric plates subjected to thermo-oxidative environments is presented. Section 3 presents model simulations. Simulations show that 0/90 unsymmetric plates are very sensitive to thermo-oxidation induced changes, thus effective for capturing the searched thermo-oxidation effects. The predictions of the present model may serve for parametric studies and experiment design. Finally, Section 4 presents conclusions and perspectives.

2. Model approach

Section 2.1 reviews the existing literature concerning thermo-oxidation in composite materials, Sections 2.2 and 2.3 are new and focus on the specific effects of thermo-oxidation on the behaviour of 0/90 unsymmetric plates.

2.1. Thermo-oxidation behaviour of polymer resins: mechanistic scheme, irreversible chemical shrinkage strain, effects of thermo-oxidation on EIT modules

As pointed out by Colin and Verdu [26] the thermo-oxidation process in epoxy matrix composites is chemically represented by the following mechanistic scheme, which take place *in the resin matrix at the molecular scale*

$$\begin{aligned}
&\mathrm{POOH} + \gamma\mathrm{PH} \rightarrow 2\mathrm{P}^{\cdot} + \mathrm{H_2O} + \nu V \ (k_1, \mathit{initiation}) \\
&2\mathrm{P}^{\cdot} + \mathrm{O_2} \rightarrow \mathrm{PO}_2^{\cdot} \ (k_2, \mathit{propagation}) \\
&\mathrm{PO}_2^{\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}^{\cdot} \ (k_3, \mathit{propagation}) \\
&\mathrm{P}^{\cdot} + \mathrm{P}^{\cdot} \rightarrow \mathit{inactive\ products1} \ (k_4, \mathit{ending}) \\
&\mathrm{P}^{\cdot} + \mathrm{PO}_2^{\cdot} \rightarrow \mathit{inactive\ products2} \ (k_5, \mathit{ending}) \\
&\mathrm{PO}_2^{\cdot} + \mathrm{PO}_2^{\cdot} \rightarrow \mathit{inactive\ products3} \ (k_6 \mathit{ending})
\end{aligned} \tag{1}$$

In this scheme the global oxidative reaction generates hydro peroxides POOH reactants and a substrate consumption phenomenon due to PH concentration. The scheme identifies ten different chemical species: POOH, PH, H_2O, V (volatiles), O_2, P., $PO_2^{\cdot}$ (the symbol **.** identifies free radicals) and three species of inactive products. Volatiles are composed by different molecules though, for convenience, only one average volatile molecule is considered. Fibres are supposed to be thermally and chemically stable through the whole process. The mechanistic scheme (1) gives the following system of partial differential equations [26]:

$$\begin{aligned}
&\frac{d[\mathrm{O_2}]}{dt} = -k_2[\mathrm{P}^{\cdot}][\mathrm{O_2}] + [\mathrm{PO}_2^{\cdot}]^2 + D_{O2}\Delta^2[\mathrm{O_2}] \\
&\frac{d[\mathrm{POOH}]}{dt} = k_3[\mathrm{PH}][\mathrm{PO}_2^{\cdot}] - k_1[\mathrm{POOH}] \\
&\frac{d[\mathrm{PH}]}{dt} = -k_3[\mathrm{PH}][\mathrm{PO}_2^{\cdot}] - \gamma k_1[\mathrm{POOH}] \\
&\frac{d[\mathrm{PO}_2^{\cdot}]}{dt} = k_2[\mathrm{P}^{\cdot}][\mathrm{O_2}] - k_3[\mathrm{PH}][\mathrm{PO}_2^{\cdot}] - k_5[\mathrm{PO}_2^{\cdot}][\mathrm{P}^{\cdot}] - 2k_6[\mathrm{PO}_2^{\cdot}]^2 \\
&\frac{d[\mathrm{P}]}{dt} = 2k_1[\mathrm{POOH}] - k_2[\mathrm{P}^{\cdot}][\mathrm{O_2}] + k_3[\mathrm{PH}][\mathrm{PO}_2^{\cdot}] - 2k_4[\mathrm{P}^{\cdot}]^2 - k_5[\mathrm{PO}_2^{\cdot}][\mathrm{P}^{\cdot}]
\end{aligned} \tag{2}$$