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Modeling the pressure dependent solubility in a thermoset resin for simulating pressure accelerated thermo-oxidation tests

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ABSTRACT

This paper presents an approach for modeling high pressure thermo-oxidative conditioning, for an epoxy resin material.

A coupled reaction–diffusion chemical "mechanistic" model of thermo-oxidation with classical boundary conditions, successfully applied for samples aged under air at atmospheric pressure but failing at high pressures, has been enhanced by formulating a new nonlinear sorption law, correlated with the results of Elastic Indentation modulus (EIT) measures at 5 bars of pure oxygen, and validated for pressures up to 8 bars of pure oxygen.

The approach allows justifying the employment of the oxygen pressure as a pertinent accelerating parameter for thermo-oxidation degradation: moreover the proposed model can be employed for the design and the optimization of accelerated thermo-oxidation tests.

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1. Introduction

Thermo-oxidation of composites is a key issue for the aeronautical industry. Indeed, the actual trend consists in increasing the amount of parts made by composite materials in aircrafts, which implies a dramatic extension of the working conditions ranges for future applications. In particular, when located close to high temperature areas (heat sources, engines...), organic matrix composites have shown to be dramatically sensitive to chemical degradation in presence of gaseous oxygen: in particular, it has been proved that the presence of oxygen enhances the kinetics of matrix microcracking during fatigue (Fig. 1, Lafarie-Frenot, 2006) or during quasi-static traction tests (Vu et al., 2013).

There exists a consistent amount of research concerning thermo-oxidation phenomena in polymers and polymer matrix composites (Vu et al., 2013; Verdu, 2012; Krasheninnikova et al., 1985; Tsotsis et al., 1999, 2001; Colin et al., 2001; Decelle et al., 2003; Colin and Verdu, 2005; Colin et al., 2005; Olivier et al., 2008, 2009; Gigliotti et al., 2011a; Ciutacu et al., 1991; Rasoldier et al., 2008; Johnson et al., 2003; Gigliotti et al., 2012, 2011b; Pochiraju et al., 2008; Tandon et al., 2005). In particular, for composite materials working within the "intermediate" temperature range (up to 200 °C), the chemical processes have been found to occur mainly in the matrix, carbons fibers being chemically and thermally stable within such range. Thermo-oxidation promotes matrix shrinkage, onset and propagation of fibre/matrix debonding, and matrix cracking (Verdu, 2012): this behavior is related to oxygen diffusion–reaction taking place from the surface exposed to the environment towards the heart of the polymer material, along a thermo-oxidized zone whose extent may be of few hundred of micrometers, leading to stiffness increase (antiplasticization phenomenon described in Verdu (2012)) and material embrittlement (Verdu, 2012). Though thermo-oxidation is basically a surface phenomenon, its effects may have dramatic impact on damage onset and propagation (Vu et al., 2013; Verdu,

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2012; Gigliotti et al., 2012); moreover, the interaction between damage and the (oxidizing) environment leads to rapid acceleration of the degradation phenomena, leading eventually to failure (Vu et al., 2013; Verdu, 2012; Gigliotti et al., 2012; Gigliotti et al., 2011; Pochiraju et al., 2008; Tandon et al., 2005).

A successful modeling of thermo-oxidation in polymer materials (particularly for epoxy resins) has been provided by Colin et al. (2001), see also (Colin and Verdu, 2005; Colin et al., 2005), who developed a reaction–diffusion coupled model in which a detailed local description of each chemical species involved in the thermo-oxidation process is given ("mechanistic" scheme). This model is somehow alternative to other different formulations (Pochiraju et al., 2008; Tandon et al., 2005), which do not enter the details of the chemistry of thermo-oxidation but employ a "reduced" model of oxygen reaction–diffusion.

The parameters of such a model have been successfully identified – at several temperatures – thanks to the employment of gravimetric tests on thick resin samples, involving the measurement of the mass globally lost by the samples during conditioning, and by qualitative and quantitative spectroscopy measures on thin polymer films, allowing detecting the type and the amount of volatile products due to chemical reactions escaping the material.

It should be noted that oxygen diffusion is in competition with chemical reaction during thermo-oxidative degradation, so that it is not obvious to characterize oxygen gradients within the material: as a matter of fact, no experimental technique is presently available for directly measuring the oxygen concentration profiles within thick samples, so that it is not possible to quantify in a direct manner the oxygen concentration gradients within the samples.

In recent work (Olivier et al., 2008), ultra micro indentation tests have been employed to provide Elastic Indentation modulus (EIT) profiles across the oxidized layer in neat resin samples and such measures have been successfully correlated to the outputs of the "mechanistic" model.

The existence of such a correlation has provided:

– A method for measuring the extent of the thermo-oxidized zone and to establish the intensity of the thermo-oxidative induced gradients close to the surfaces exposed to the environment.
– A route for validating the pertinence of the model approach in Colin et al. (2001).

This approach has been fully exploited in the case of 977-2 epoxy resin samples conditioned under air at atmospheric pressure (Olivier et al., 2008): in particular, within the framework of a one-dimensional model, the classical "mechanistic" scheme has been employed to calculate the evolution of the concentration of oxidation products, Q (see reference Colin et al. (2001) and Section 2 later in this paper for an exhaustive definition of such a variable), across the oxidized layer, as a function of the distance from the edge exposed to the environment, for a sample conditioned under atmospheric air, at 150 °C, for three different ageing durations (100 h, 600 h and 1000 h) (Fig. 2a, Lafarie-Frenot, 2006).

The calculated Q has been correlated with the EIT measured along the oxidized layer (Fig. 2b, Lafarie-Frenot, 2006) and a phenomenological relationship between the computed Q and the measured EIT (Fig. 3 Lafarie-Frenot, 2006) has been established.

The low dispersion of the data around the mean curve of Fig. 3 is an evidence of the "physical" origin of this correlation.

This result of great importance since, for the first time concerning thermo-oxidation, a quantitative description of the EIT evolution is available at any point in the sample and anytime during the oxidation phase. Moreover, since it can be measured experimentally and locally, the EIT becomes a good indicator of thermo-oxidation and can be employed for testing the coherence of the numerical predictions.
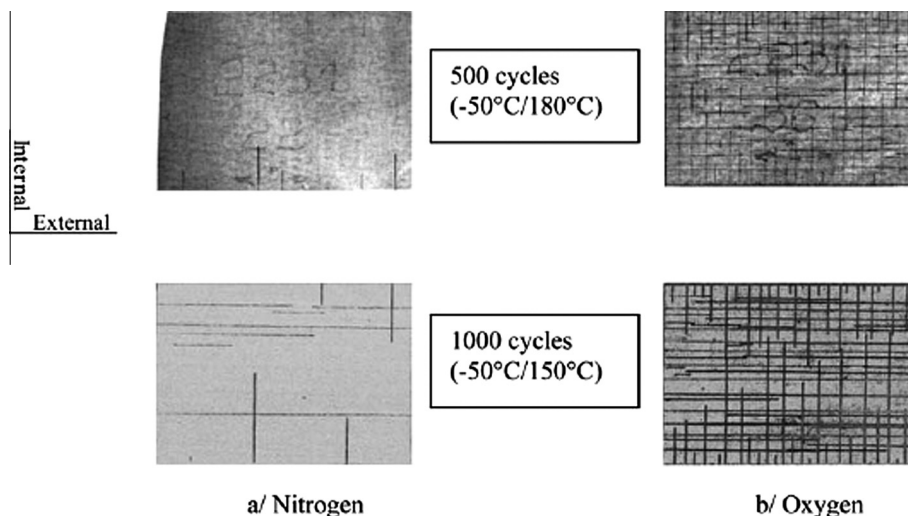

Fig. 1. Comparison of $[0_3/90_3]_s$ samples X radiographs according to the environment and to the amplitude of the thermal cycling test (Lafarie-Frenot, 2006).