



Thermo-oxidative induced shrinkage in Organic Matrix Composites for High Temperature Applications: Effect of fibre arrangement and oxygen pressure



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ABSTRACT

The present paper focuses on thermo-oxidative induced chemical shrinkage in HTS/TACTIX carbon/epoxy Organic Matrix Composites for High Temperature Applications, providing an insight on the effect of the fibre arrangement and of the oxygen pressure as an accelerating parameter. In particular, measurement of matrix shrinkage in composites surface is carried out by Interferometric Microscopy for virgin samples (initial state) and for samples aged under oxygen pressure and air at atmospheric pressure: some discussion about the “structural” effect (arrangement of fibres, fibre volume fraction) on matrix shrinkage development of unidirectional composites is provided; a link between the measured surface matrix shrinkage and the evolution of the surface elastic indentation modulus measured in pure resin samples can be clearly established: moreover, it is shown that matrix shrinkage development in composites can be conveniently accelerated by the employment of oxygen pressure, as in pure resin systems.

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1. Introduction

Organic Matrix Composites (OMC) may suffer from thermo-oxidation phenomena at intermediate/high temperatures, that is – for epoxy systems with glass transition temperature, T_g , values of around 200 °C – starting from around 100 °C. Thermo-oxidation is responsible for degradation of the matrix system and the study of the polymer ageing mechanisms is a preliminary step in order to characterize the degradation of the composite. It has been widely shown by research studies on pure resin systems [1–6] that thermo-oxidation leads to the occurrence of a thin degraded layer (few hundred of microns, depending on the material), starting from the external surface exposed to the environment to the heart of the sample, in which physical–chemical and material property (composition, colour, shrinkage strain, stiffness, strength, toughness, ...) gradients arise. Mechanical property gradients have been characterised by local ultra-micro indentation tests, leading to the measurement of local elastic indentation moduli (EIT) [7–9] and to the establishment of local mechanical constitutive laws [9,10], eventually depending on ageing. Such studies have been supplemented by detailed analyses of the local physi-

cal–chemical effects of thermo-oxidation on the polymer system, and a clear link between mechanical and physical–chemical property changes has been established. A detailed account of such behaviour is given, for instance, in [11]. In fact, oxygen diffusion/reaction within the polymer material promotes chain scission and antiplasticization of the polymer system, leading to chemical shrinkage (related to departure of volatiles produced by the thermo-oxidative reaction) and increase of the elastic modulus at temperatures lower than T_g (glass transition temperature). It has been successfully proven [8,9] that the measure of the relative change of EIT (with respect to the initial virgin value) is a good indicator of the thermo-oxidative reaction/diffusion process. Moreover, the employment of EIT measures allows validating the use of oxygen pressure as a way to accelerate thermo-oxidative phenomena [12], in agreement with the thermodynamics chemistry of irreversible processes [13]. On the other hand, the measurement of chemical shrinkage promoted by thermo-oxidation is not an easy task, though some techniques have been proposed [14]; the main difficulty resides in the fact that shrinkage strain is difficult to measure locally, so that values measured on macroscopic samples tend not to be conclusive.

When thermo-oxidation of carbon fibre OMC is concerned, since carbon fibres are reasonably inert to oxidation (at least for ageing temperatures below 300 °C) the degradation effects concern

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the polymer matrix only [15,4,16,17], more or less at the same extent than the pure resin.

Some recent studies have focused on carbon-epoxy matrix systems, addressing the effect of the fibrous reinforcement on the degradation of the composite, both at the microscopic and the macroscopic scale [18,19], including braided textile systems [20].

Though it is claimed that the presence of carbon fibres (particularly the carbon atoms at the fibre/matrix interfaces) may modify matrix degradation, but results on these effects are not conclusive and strongly depend on the composite system [15,4]. Pochiraju and Tandon [17] have studied thermo-oxidation of high temperature polymer matrix composites indicating some modelling routes for such material systems: from these studies, it is evident that the main ingredients for thermo-oxidation modelling in composites are the property changes and chemical shrinkage promoted by ageing; the latter play a fundamental role in the establishment of residual strain/stress in the composite, leading eventually to the occurrence of damage. By using Interferometric Microscopy, Vu et al. [21] have carried out a systematic study on matrix shrinkage on the surface of thick unidirectional IM7/977-2 carbon/epoxy composites subjected to aggressive thermo-oxidative environment, under air at atmospheric pressure or under oxygen partial pressure up to 5 bar, shedding some light about the chronology of matrix shrinkage and damage development in such composite systems. It was shown that matrix shrinkage between fibres increases with conditioning time particularly in resin rich zones (zones with low fibre volume fraction). It is in these zones that damage in the form of debonding at the fibre/matrix interfaces first occurs. Since fibres do not deform with ageing, they constrain the free development of matrix resin shrinkage; however this effect – which can be rightly qualified as “structural” – is more marked in resin rich zones, since matrix deforms more severely in these zones.

The present paper puts forward the analysis initiated by Vu et al. [21], applying a similar methodology for a HTS/TACTIX carbon/epoxy composite system. The main aim of the paper is to provide additional explanation over the “structural” effect (arrangement of fibres, fibre volume fraction) on matrix shrinkage development of unidirectional composites. Incidentally, a link between the measured surface matrix shrinkage and the evolution of the surface EIT measured in pure resin samples can be clearly established: moreover, it is shown that matrix shrinkage development in composites can be conveniently accelerated by the employment of oxygen pressure, as in pure resin systems.

The paper is organised as follows: Section 2 presents the material, sample preparation and experimental technique, Section 3 focuses on measurement of matrix shrinkage in composites surface by Interferometric Microscopy for virgin samples (initial state) and for samples aged under partial oxygen pressure and air at atmospheric pressure, with related discussion. Finally, Section 4 presents some conclusions and perspectives.

2. Material, specimen preparation and experimental technique

The material employed for this research is a HTS/TACTIX carbon/epoxy provided by Airbus Group Innovation (Suresnes). The main physical properties of such material – as provided by the supplier – are collected in Table 1; it can be noted, in particular, that the resin content within the composite is around 34% and that the polymer glass transition temperature (T_g) is between 190 °C and 250 °C (measured by DMA), depending on the properties of the hardener. The optimised polymerization cycle of the composite pre-preg consists of a gel phase of 1 h at 140 °C, a first curing dwell of 3 h at 180 °C and a second curing dwell of 1 h at 250 °C. The material then undergoes a post-curing dwell under vacuum of

Table 1
Physical properties of the HTS/TACTIX composite.

Property	Value
Fibre density	1.78 g/cc
Crosslinked resin density	1.31 g/cc
Volatiles	0.02%
Surface mass of the pre-preg	222.9 g/m ²
T_g	190–250 °C
Resin content	34.3%

10 h at 230 °C, necessary to provide a crosslinking rate close to 100%.

Ageing of the composite samples is performed by employing the pressurized COMEDI instrumented setup available at the PPRIME laboratory (Maximum temperature: 200 °C, maximum pressure: 10 bar, environment: air, oxygen, nitrogen).

Preliminary tests on the pure resin [22] have shown that the employment of moderate oxygen pressures is effective to accelerate thermo-oxidation phenomena, while ageing under nitrogen inert environment – even at high pressure – do not promote any thermal ageing of the material.

To measure matrix shrinkage a Taylor & Hobson Talysurf CCI 6000 Interferometric Microscope is employed: the measurement principle of such apparatus is based on light interference, according to the following steps:

- A coherent light is simultaneously sent to a reference mirror and to the sample surface: the focal distance of the device defines the focusing plane on the sample surface.
- The light is reflected by the observed sample and by the reference mirror.
- The reflected rays converge on a CCD camera, where the interference takes place.
- Positioning the focal plane of the lens at different levels of the sample surface, it is possible to extract a series of images containing the three-dimensional representation of the observed object.
- Finally, a post-processing software reconstructs a digital image of the observed surface.

The vertical lens shift is imposed by a piezoelectric actuator, with a vertical spatial resolution of 0.01 nm: the measuring range and spatial resolution depend on the objective magnification. In this study a 50× magnification is used, allowing observing an area of 360 μm × 360 μm with an in-plane spatial resolution of about 0.35 μm. By employing such optical parameters surface slopes higher than 27.7° with respect to the horizontal plane cannot be measured. This limitation – intrinsic to the device – has been extensively studied by Vu et al. [21] when studying matrix shrinkage profiles in UD composite surfaces: these authors have shown that debonding at the fibre/matrix interface is given by the device as “unmeasured” points, since in this case the local slope largely exceeds the limit of 27.7°.

HTS/TACTIX composite samples (Fig. 1a) with dimensions 15 mm × 15 mm × 10 mm were cut from a thick unidirectional plate (50 plies). One of the surfaces orthogonal to the fibre direction was polished using the protocol detailed in Table 2 (surface polished up to 1 μm). Fig. 1 illustrates the result of the polishing phase and the details of the measurement technique, based on observation by Interferometric Microscopy (IM) of a specific location of the polished surface. The exact position of this location was identified with respect to a corner of the sample, since the IM apparatus allows imposing automatic displacements along the x and the y axes, in a highly reproducible way (Fig. 1b). In this case, along each axis, a displacement of 2 mm with respect to the bot-

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