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Effect of Thermo-oxidation on the local mechanical behaviour of epoxy polymer materials for high temperature applications

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ABSTRACT

This paper presents an original coupled experimental/numerical approach for the characterization of the effects of thermo-oxidation on the local mechanical behaviour of aged polymer materials. The experimental approach is based on ultra-micro indentation (UMI) and interferometric microscopy (IM) tests. The UMI load vs. displacement curve is exploited to gain some information about the material behaviour at the short-range timescales, the IM measurement of the three-dimensional indentation print and of its evolution with time allows characterizing the material behaviour at the long-range timescales. The numerical approach is based on an ageing dependent nonlinear viscoelastic/softening constitutive law developed within the framework of the Thermodynamics of Irreversible Processes (TIP) with Internal Variables (TIV). The constitutive law is integrated within a 3D ABAQUS® finite element model of the test setup and the parameters of the law are identified for different ageing conditions.

1. Introduction

Ageing of polymer materials exposed to thermo-oxidative environment develops at a local scale (micrometric scale or lower), since the degradation mechanisms concern the macromolecular structure (Colin, and Verdu, 2005): due to the local nature of the involved physical phenomena, material property gradients develop over a length of few microns (Tandon et al., 2005; Tandon et al., 2006; Pochiraju, and Tandon, 2006; Olivier et al., 2008; Tandon et al., 2009, Lafarie-Frenot et al., 2010). In order to gain pertinent information about the polymer degraded mechanical properties at such scales dedicated tests must be carried out: classical tests – such as uniaxial traction/compression or DMA tests on “macroscopic” samples – are difficult to analyse and are sometimes not conclusive (Lafarie-Frenot et al., 2010).

Thermo-oxidative ageing of polymer materials occurs at intermediate/high temperature (sometimes well below the polymer glass transition temperature); it has been demonstrated that thermo-oxidation induces a change in mechanical properties, which is related to the polymer chain scission phenomena due to oxygen reaction-diffusion (Verdu, 2012): this change takes place at a local scale and it is strictly related to the oxygen diffusion-reaction concentration profiles (Olivier et al., 2008).

The present approach aims at characterizing the time-dependent mechanical behaviour of virgin and aged epoxy polymer materials and is based on ultra-micro indentation (UMI) and interferometric microscopy (IM) tests: the UMI load vs. displacement curve is exploited to gain some information about the short-range timescales, the IM observation of the three-dimensional indentation prints and of their evolution with time allows characterizing the long-range timescales (Minervino et al., 2013).

The numerical approach provides simulation of the experimentally observed behaviour by integrating a nonlinear viscoelastic/softening polymer constitutive law within a 3D ABAQUS® (Dassault Systèmes Simulia Corp 2009) finite element model of the test setup. The constitutive law is modeled within the framework of Prigogine’s fluctuation theory and is based on the thermodynamics of irreversible processes (TIP): it represents an enhanced version of the behaviour model presented by the same authors (Gigliotti et al., 2011; Minervino et al., 2014).

The identification of the material parameters characterizing the constitutive law – for both virgin and aged materials - is carried out by inverse analysis of the experimental results through the open-source optimization code DAKOTA® (Laboratories, 2009).

Characterisation of thermo-oxidative ageing of elastomers has been provided in Johlitz, and Lion, 2013; Johlitz et al., 2014; Herzig et al., 2014, who employed a continuum rational thermodynamics based approach to develop an ageing dependent material constitutive law. In that case traction tests have been employed showing that thermo-oxidation may have consistent impact on the macroscopic materials response.

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The present approach is slightly different: as mentioned - the model is developed within the framework of TIP - conceptually different from rational thermodynamics, then indentation tests are employed and associated to a close following of the recovery behaviour of the indentation print. Therefore, in the present case, the material is loaded by a three-dimensional tri-axial compressive solicitation, close to that often encountered by polymer matrices confined between rigid fibrous reinforcements in composite materials.

As a matter of fact, consistent research work has been devoted to the development of behaviour law of polymer materials under compressive solicitation related to indentation test, at the local scale (Govaert et al., 2000; Kermouche et al., 2008; Rauchs, and Bardon, 2009; Tervoort et al., 1996; Tervoort et al., 1997), for glassy polymers (PMMA, PS and PC samples) and rubber compounds tested by spherical indentation (Rauchs, and Bardon, 2009).

At a macroscopic scale, the constitutive behaviour of glassy polymers has been investigated, for instance, in Arruda, and Boyce, 1993; Arruda et al., 2001; Boyce et al., 1988; Mulliken, and Boyce, 2006; Karra, and Rajagopal, 2009; Karra, and Rajagopal, 2011; DeSimone et al., 2001; Simo, 1987. DeSimone et al. (DeSimone et al., 2001) and Simo (Simo, 1987) studied the softening behaviour of rubber under deformation, the so-called Mullins' effect: DeSimone et al. (DeSimone et al., 2001) linked the elastic modulus decrease with an internal damage-like variable, depending on strain.

The literature agrees in concluding that:

- Polymers may exhibit different material behaviour depending on the tested scale (the polymer constitutive laws developed at a given scale may not be conclusive for reproducing the mechanical behaviour at another scale) and on the imposed solicitation,
- It may be hard to characterise the long-time material response of polymer materials and to follow its recovery behaviour,
- Few information – if none – is available concerning the evolution of the mechanical behaviour (full constitutive law) with ageing.

The present paper tries to put some light on the last two questions, while keeping the first question substantially unanswered.

The paper is organised as follows:

- Section 2 presents the tested material, specimen preparation and the experimental technique,
- Section 3 presents experimental results illustrating the evolution of the polymer mechanical behaviour during isothermal ageing observed by local indentation tests,
- Section 4 presents the definition of a dedicated variable for the description of the thermo-oxidation phenomena,
- Section 5 presents the ageing dependent polymer constitutive law, integrating the introduced variable as an internal variable for the developed material model, and the fundamental of the numerical/experimental approach, recalling the information given in Minervino et al., 2014,
- Section 6 presents parameters identification for several ageing levels by inverse analysis of the experimental results,
- finally, Section 8 collects final remarks and conclusions.

The final aim of the present research is to integrate the identified ageing dependent constitutive law and the related property gradients into more complex structural configurations (unidirectional composite materials, Vu et al., 2012; Gigliotti et al., 2016, composite laminates, textile composites, structured materials) in order to better interpret experiments carried out on such structures (Gigliotti et al., 2016) and to perform predictions at several structural scales.

2. Material, specimen preparation and experimental technique

The studied material is a high-temperature high-performance epoxy resin (referred to as "Epoxy resin" for confidentiality reasons) developed to work in a temperature range between 150°C and 200°C. Its glass transition temperature - as obtained by Dynamical Mechanical Analysis (DMA) tests performed in single cantilever bending mode - is around 250°C, the glass transition temperature corresponding to the loss modulus spectrum peak at high temperature.

All specimens (initial dimensions $30\,mm \times 10\,mm \times 2\,mm$) were initially dried in a vacuum oven at 80°C. Then, isothermal ageing was carried out in an oven at 150°C under air at atmospheric pressure and 2 bar of oxygen pressure. The employment of oxygen pressure as an acceleration parameter for thermo-oxidative degradation phenomena (Tsotsis et al., 1999; Tsotsis et al., 2001; Astruc et al., 2004; Ciutacu et al., 1991) has been studied and validated in (Grandidier et al., 2015), at least for pressure values up to 8 bar.

Fig. 1 shows the procedure for preparing virgin and aged specimens (Minervino et al., 2013):

- The specimen is first cut in the middle perpendicularly to the exposed surface (Fig. 1a) in order to get access to the core of the material, which is less affected by oxygen reaction/diffusion phenomena. The observed surface, on which indentation tests are performed, is presented in Fig. 1b,
- The two parts of the specimen are, then, placed side-by-side, coated, and finally polished by a semi-automatic polishing machine to get a clean and smooth indentation surface, according to Olivier et al., 2008. The final sample is shown in Fig. 1c,
- Fig. 1d shows an optical microscopy image of the aged sample surface, for an Epoxy 2 specimen aged 72 h at 150°C under 2b of O_2. The oxidized layer can be easily distinguished from the non-oxidized core of the polymer. The usual procedure/criterion to identify the oxidized layer is described in Colin et al., 2005 and Tandon et al., 2009; in this case, the two zones (one aged, the other virgin) are recognized thanks to the different appearance of their surfaces, related to their different superficial hardness. In the present approach the identification of an oxidized layer is based on the recognition of a strained zone, in which a gradient of both mechanical properties and residual strains of chemical origin develops. This zone can be observed by optical microscopy (Fig. 1d, see also Fig. 2a) and by Interferometric Microscopy (IM, Fig. 2b). As clearly shown in Fig. 2, close to the surface exposed to the environment, the thermo-oxidized layer presents some surface distortion related to mechanical property gradients and chemical residual strains Therefore, it is not easy to measure the oxidized layer thickness: according to a pure optical criterion, in this case, this thickness is around 150 μm.

The thermo-oxidative affected polymer mechanical behaviour has been characterized by two local tests. Fig. 3 shows the experimental technique (more details about this technique are provided in Minervino et al., 2013:

- Ultra micro indentation (UMI) tests have been performed on the polished surface at different distances from the directly exposed surface, Fig. 3a;
- during the indentation test the full indentation curve has been recorded, Fig. 3b;
- the full 3D indentation print shape has been measured by IM (Fig. 3c) at regular time intervals, from few minutes after the indentation test up to three months.

In this work, the instrumented Ultra-Micro Indentation device Fischerscope® H100C, equipped with a Vickers diamond indenter