IDENTIFICATION OF THE THERMO-OXIDATIVE AFFECTED MATERIAL PROPERTIES OF POLYMERS FOR HIGH TEMPERATURE APPLICATIONS BY A COUPLED EXPERIMENTAL/NUMERICAL APPROACH

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Abstract
Thermo-oxidation of organic resins is a coupled diffusion-reaction phenomenon taking place within the oxidation sites present in the atomic structure of the matter. Oxidized samples may exhibit sharp property gradients usually condensed in a thickness of a few tens of microns. In this paper, we propose a local Ultra-Micro Indentation (UMI) test to characterize the thermo-oxidative induced property changes in polymers for high temperature applications. The characterization is carried out by inverse analysis, by coupling UMI measures with finite element model simulations. A numerical non-linear 3D model has been developed employing the ABAQUS [1] commercial software: by comparison between the model simulations and the typical load-displacement indentation curves the thermo-oxidative affected material constitutive law can be fully identified.

1 Introduction

In order to reduce the weight of aerospace structures, organic matrix composites (OMC) are progressively replacing metallic materials in a temperature range between -50°C and 250°C. Exposure to "high" temperatures of OMCs (in all cases below the resin glass transition temperature) requires deep understanding of the degradation phenomena occurring at these temperatures.

Thermal oxidation of organic resins [2, 3] is a coupled phenomenon of diffusion-reaction taking place in the oxidation sites present in the atomic structure of matter [4]. Several studies have been carried out in order to properly model the various physical and chemical aspects of materials degradation [5-7]. A mechanistic model [4], tracing the evolution of the different species concentration, has been developed to link the oxidation effects to the chemical equations.

Thermo-oxidation of organic resins can lead to the appearance of surface damage, without any applied external load [2, 3]. At the macromolecular level material embrittlement is mainly due to the change of atomic structure in the oxidized layer (splitting of chemical bonds). On the other hand thermal oxidation causes a local variation of density and mass, the formation of

shrinkage strains [8] and local increase of the resin elastic modulus (EIT) [9], which leads to residual stress, damage onset and material degradation [9, 10].
Depending on its size, the oxidized sample may exhibit sharp property gradients, starting from the surface – directly exposed to the environment – to the heart, less affected by oxygen reaction-diffusion. Usually this gradient is condensed in a thickness of few tens of microns, which underlines the clearly local nature of the phenomenon. In this regard the classical tensile, compressive or shock tests are not able to take into account the changes in material behaviour following up oxidation; the aging affected layer is usually small with respect to the specimen dimensions and the tests results tend to be not conclusive. In addition, as shown by [11-15], it is hard to take into account both the macroscopic and the microscopic material behaviour by a unique constitutive law.
The final aim of this paper is to develop a numerical/experimental approach in order to characterise the thermo-oxidative induced property changes in polymers for high temperature applications at the same local scale of oxidation phenomenon. The experimental approach is based on two local tests:

- Ultra-Micro Indentation (UMI) tests, allowing measuring the thickness of the oxidized layer, the embrittlement of the aged polymer and the viscoelastic material behaviour. Compared to classical tests, the benefits of UMI tests are many and various: the scatter of results is very low and the matter can be tested locally, revealing material non-homogeneities. The UMI measurements are performed on aged high-performance high-temperature resins at different sites along a direction perpendicular to the exposed surface,
- Confocal Interferometric Microscopy (CIM) measurements, allowing following the evolution of 3D indentation prints over time and characterising the long-time viscoelastic material behaviour.

Material characterization is carried out by inverse analysis, by coupling experimental tests with finite element simulations. A numerical non-linear 3D model has been developed employing the ABAQUS [1] commercial software: by comparison between model simulations, “load vs. penetration depth” indentation curves and indentation prints shape evolution over time, the thermo-oxidative affected material constitutive law can be fully identified.
In section 2 aging effects on the material behaviour are experimentally carried out by classical UMI tests, progressive UMI tests and CIM measurements. Section 3 describes the model approach and shows the perfect agreement between the numerical simulations and the experimental results for all indentation test condition changes. Section 4 presents final remarks and conclusions.

2 Material properties identification by ultra-micro indentation test

In this study we have used the UMI Fischerscope® H100C setup to characterize material mechanical properties evolution. The device is equipped with a Vickers diamond indenter whose cartography is known, and it has a testing load range from 0.4mN to 1000mN.
During the indentation test, the testing force F and the penetration depth h are recorded and the typical “load vs. penetration depth” curve is plotted. Starting from this curve, showed in Fig. 1, some local mechanical properties could be identified, according to 14577 ISO standard. For simplicity in the following the “load vs. penetration depth” curve will be called “indentation curve”.

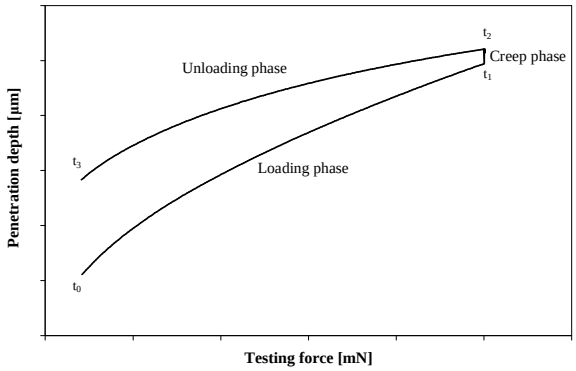

Figure 1. Typical "load vs. penetration depth" curve for a polymer.

In the indentation curve three main phases are discernible: the loading phase ($t_0 \le t \le t_1$), the creep phase ($t_1 \le t \le t_2$) and the unloading phase ($t_2 \le t \le t_3$). During these phases the most important calculated parameters are: the Vickers hardness HV (Eq. 1), which is the ratio between the load $F_{\max}$ expressed in Newton and the indentation surface area expressed in square millimetres, the indentation creep parameter *CIT* (Eq. 2), defined as the relative penetration depth variation, and the "indentation elastic modulus" *EIT* (Eq. 3), calculated from the slope of the indentation curve at $F_{\max}$.

$$HV = \frac{F_{\max}}{A_S} \tag{1}$$

$$CIT = \frac{h_2 - h_1}{h_1} \times 100 \tag{2}$$

where h_1 and h_2 are, respectively, the indentation depth at t_1 and t_2.

$$EIT = \frac{\sqrt{\pi}\left(dF/dh\right)}{2\beta\sqrt{A_p}} \tag{3}$$

where β depends on the indenter type ($\beta = 1.013$ for a Vickers indenter) and A_p is the contact area between the indenter and the sample, projected on a plane perpendicular to the indenter axis.

These classical indentation parameters are not able to fully describe the material behaviour: in some cases, they have scarce physical sense and tend to change with respect to the maximum testing load. However, Olivier et al. [9] have found a link between the EIT modulus and the chemical oxidation parameters and, supposing the Young modulus to have the same relation with respect to the oxidation phenomenon, they were able to couple mechanical and chemical evolution during aging.

On the other side since we want to identify the thermo-oxidative affected material properties directly starting from this local test, the indentation curve is full of information; all changes in mechanical properties – due to aging – are expressed by different indentation curves. During the UMI test a load can be applied in a very local area leading to have high strains whose gradient are located in few microns. Firstly, in this small region we can reasonably consider also an aging resin as a homogeneous material, being at the same scale of the oxidation

effects. Secondly, throughout the UMI test, strains grow up to a level which cannot be reached by classical compression or traction test.
Before UMI tests, high-performance high-temperature polymer resin specimens were dried in vacuum four days at 80°C, represented the non-oxidized state. Then they were aged in an isothermal environment at 150°C in ambient air or under oxygen pressure – typically 2 bars – for different durations. Aged specimens were cut and coated, and finally polished by a semi-automatic polishing machine to get a clean indentation surface, according to [9].
Fig. 2 shows the indentation curve changes due to thermo oxidation at a distance of 20 µm from the directly exposed surface. The oxidized specimen has been aged for 72 hours at 150°C under 2 bars oxygen pressure while the reference specimen has been only dried. The indentation tests were carried out without the creep phase and the maximum testing load (5mN) was reached in 20 seconds.

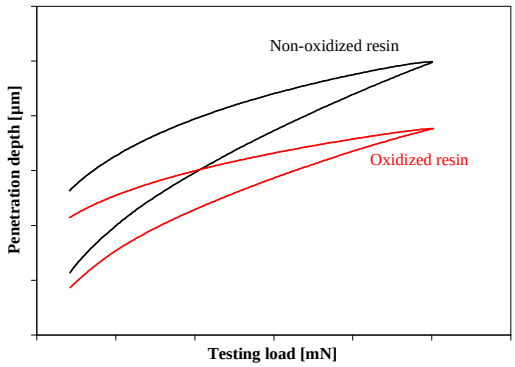

Figure 2. The effects of oxidation on the indentation curve.

For the oxidized resin, the maximum testing load corresponds to a lower penetration depth, indicating a sharp increase of the material stiffness. Since the polymer does not exhibit a perfect elastic behaviour, a difference between loading and unloading paths can be appreciated. For metals this difference is mainly due to plasticity, but for polymers the physical interpretation is more complex: it could be linked to viscosity and it seems to be affected by oxidation. To exclude any plasticity, confocal interferometric microscopy (CIM) measurements have been performed.

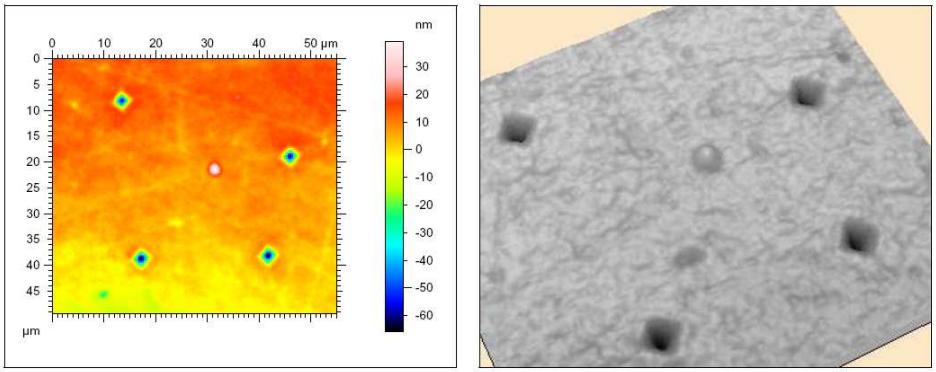

Figure 3. Specimen surface about 30 minutes after the indentation test.

CIM method allows quantitatively measuring the profile of the sample surface. The used setup is the Talysurf CCI 6000 developed by Taylor Hobson. The measurement method is based on the light signals interference. A uniform-produced light signal is reflected both on a reference mirror and on the matter surface. Light interference occurs on a CCD camera. By

moving the objective vertically via the high precision piezoelectric actuator, an interference spectrum for each CCD camera pixel is obtained. At last, the post-processing software identifies the maximum of the spectrum by image correlation and rebuilds the 3D surface.
Indentation prints are observable on CIM. In Fig.3 the surface of a non-oxidized resin about 30 minutes after the indentation test is presented.
Indentation prints evolution is followed up to 3 months and the indentation depth as a function of time is plotted if Fig. 4, for non-oxidized and oxidized resins: relaxation behaviour can be noted.

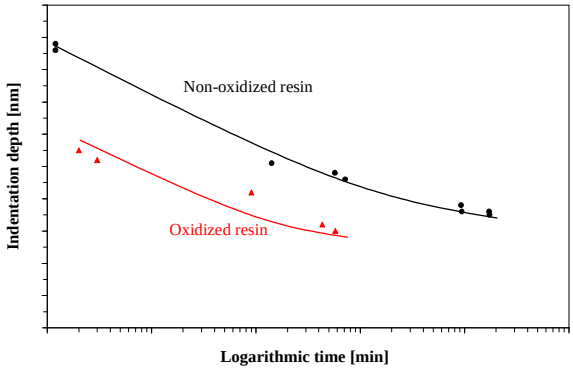

Figure 4. Evolution of the indentation depth over time.

A difference between the two relaxation curves is evident, although they seem to target the same final value. In order to calibrate the long-time relaxation behaviour in the numerical model this tool will be indispensable both for non-oxidized and oxidized resins. Unfortunately, the time to achieve a stabilized state is long, but the phenomenon is strongly influenced by temperature. Therefore, a non-oxidized specimen was placed in a vacuum oven at 150°C (below its glass transition temperature that is about 250°C). It is very important to work under vacuum because resin oxidation is fast at such temperature. After about 10 minutes in oven, specimen surface was re-observed at the CIM without finding any indentation print, while polishing rows and surface damages were still visible, as shown in Fig. 5.

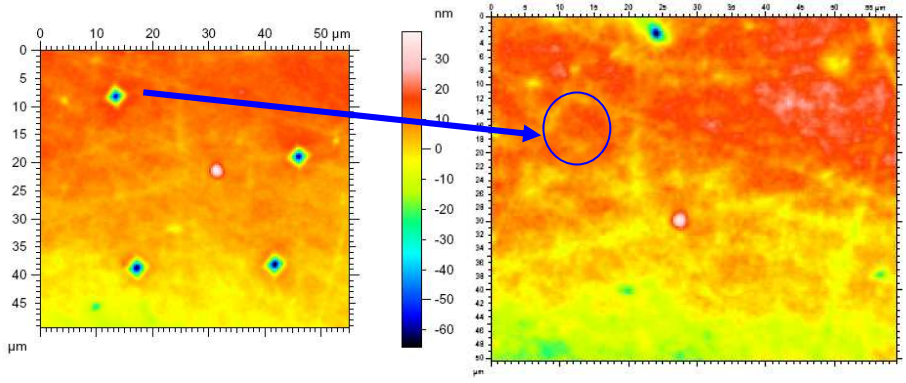

Figure 5. Left: After-indentation specimen surface. Right: Specimen surface after 10 minutes in a vacuum oven at 150°C.

In order to complete the experimental study of polymer behaviour, Fig. 6 shows what happens when indentation test conditions are changed.

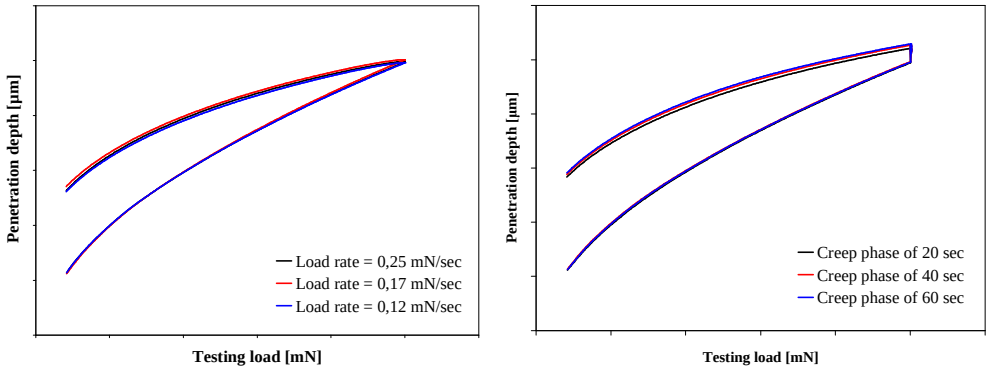

Figure 6. a. Non-oxidized resin indentation curves for different load rates in loading phases. b. Non-oxidized resin indentation curves for different creep phase durations.

Fig. 6a shows that the load rate doesn't influence the indentation curve, while in Fig. 6b an augmentation of penetration depth for different creep phase durations (20, 40 and 60 seconds) is observed. Therefore, material evolution doesn't seem to be linked to strain rate while viscoelastic effects are not negligible and indentation test proves to be a good tool to study short-time relaxation.
Finally the load vs. time testing condition has been amended to provide progressive loading phases at several intermediate levels, unloading up to 20% of the maximum reached load.

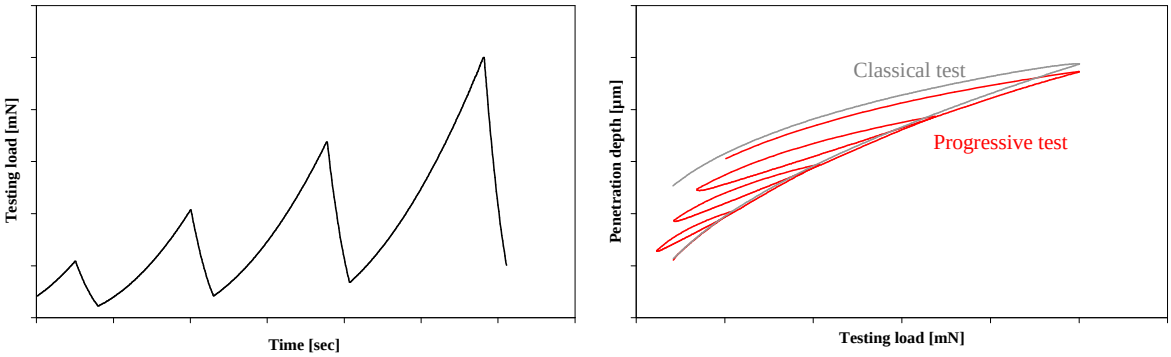

Figure 7. a. Load vs. time testing condition. b. Comparison between classical and "progressive" indentation testing conditions.

Fig. 7 shows the load vs. time testing condition (a) and a comparison between classical and "progressive" indentation conditions (b), for the non-oxidized resin. The "progressive" indentation curve loops are a good indication of the polymer hysteretic behaviour that will be taken into account in the constitutive law.

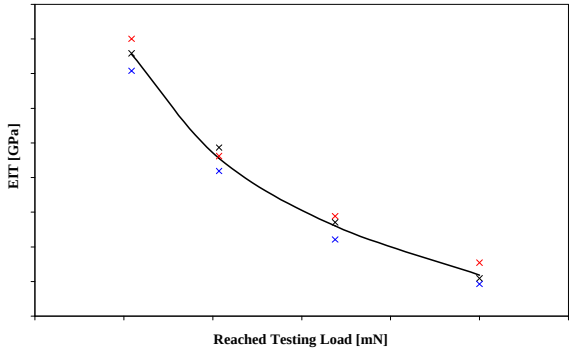

Figure 8. EIT evolution over indentation test for three non-oxidized specimens.

In addition, three independent indentation tests on three different non-oxidized specimens have found a link between the intermediate reached load and the EIT modulus decrease, as shown in Fig. 8.

3 Numerical model

At this local scale material behaviour turns out to be far from that one exhibited in a tensile or compression standard test. During the UMI test strains are very high and resin viscoelasticity is considerable, already at room temperature. Long-time relaxation could be identified at room temperature by the experimental indentation prints relaxation. Moreover, indentation prints on the non-oxidized resin vanish after 10 minutes at 150°C suggesting the absence of plastic strain. According to progressive indentation test, EIT modulus decreases throughout the loading phase as well as hysteretic loops are observable.
Due to the complexity of the indentation test results, the development of a numerical 3D model is essential for a correct interpretation of the material behaviour.
A 3D model has been developed by employing the ABAQUS commercial software [1] (Fig. 9): it is composed by 13500 20-node quadratic brick reduced integration elements.

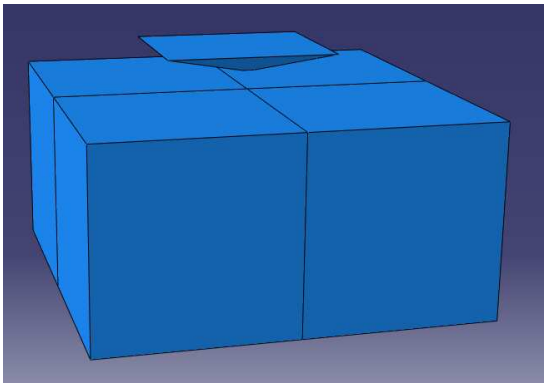

Figure 9. 3D ABAQUS model of the indentation test.

A first numerical/experimental comparison is shown in Fig. 10, where the model results are in good agreement with respect to the experiments, both for short-time and long-time tests.

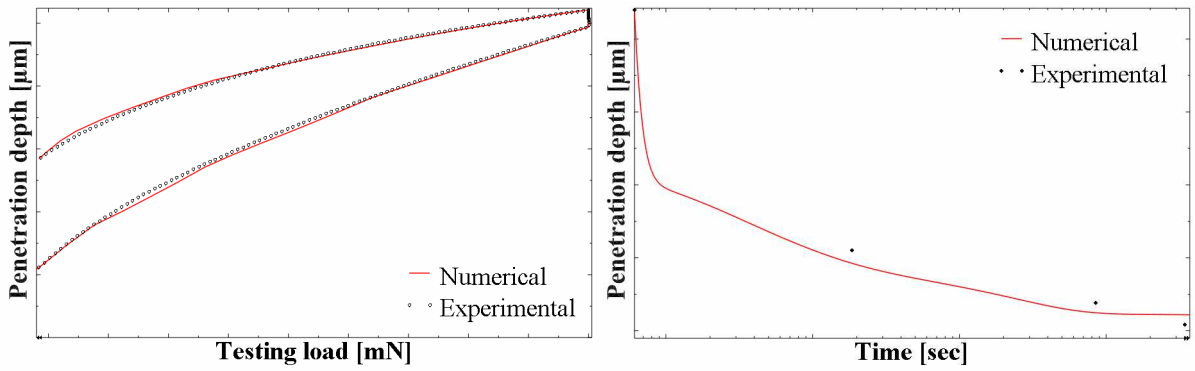

Figure 10. Numerical/experimental comparison for non-oxidized resin classical indentation test.

A constitutive law taking into account all the presented effects has been developed by employing dedicated FORTRAN subroutines.

4 Conclusion

In this paper a numerical/experimental approach for studying the oxidative polymer properties evolution has been presented. Since the scale at which UMI tests are performed is very local,

the aging effects (acting at the same scale) on the indentation and relaxation curves are considerable. So, the UMI test proves to be an important tool for studying polymer thermo oxidation. Numerical model material properties have been identified only for the non-oxidized resin, showing a good agreement with respect to the experimental results for all the explored indentation test conditions. The numerical study will be extended to the oxidized resin in order to find a link between the material mechanical properties and the oxidation phenomenon.

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