METHODOLOGY TO CHARACTERIZE THE INFLUENCE OF THERMAL AGEING ON STRENGTH PROPERTIES OF EPOXY COMPOSITE MATRICES.

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Abstract
The purpose of this communication is to propose a methodology to evaluate the influence of thermal ageing oxidation on epoxy strength properties. Since oxidation is confined in a thin layer of the surface of bulk samples, mechanical properties and strength could not be measured easily. To address this problem, we propose to characterize the oxidized layer thickness and gradient of elastic properties by means of Ultra-Micro-Indentation (UMI) tests and its strength properties by conducting 4-points bending tests to mainly stress its outside oxidized layers.

1. Introduction

The increasing use of polymer composites in aeronautical structures has revealed the need to extend their domain of use to higher temperatures. For long term conditions, thermal ageing, and in particular thermo-oxidation of the matrix, should be considered. This phenomenon occurs in a thin layer from the surface exposed to the environment and modifies locally the mechanical and physical properties of the resin [1,2]. The oxidized layer is responsible of damage initiation and degradation of strength properties of the composite [3].

The initiation of damage in the oxidized layer is due to complex mechanisms that involve chemical shrinkage, modification of viscoelastic properties and embrittlement of the resin [4,5,6].

Considering that these modifications vary gradually from the surface and increase with time, very specific tests should be conducted to measure the influence of oxidation on mechanical properties of bulk resin specimens. In [7], authors conducted local microindentation tests to measure the gradient of elastic properties in the oxidized layer of an epoxy resin for different ageing conditions. Thanks to this technique, they also characterized the evolution of the oxidized layer thickness with ageing time under oxygen and air conditions and demonstrate that it is possible to accelerate the thermal ageing by increasing oxygen pressure. In recent work, Minervino [8] proposed to identify viscoelastic behavior of the oxidized resin by

measuring the evolution of the force/displacement curve during microindentation test combined with a dedicated numerical approach.

Fayolle [9,10] studied the thermo-oxidation of polypropylene on 100 µm thin films in which ageing is not controlled by the diffusion of oxygen. In that case the degradation is homogeneous. To study the influence of oxidation on fracture properties, dogbone notched specimens were used to measure the essential work of fracture of virgin and aged specimens. In [11], the authors measured the molar mass changes due to oxidation and identify a critical molar mass for which embrittlement leads to ductile to brittle transition. The authors has also observed that in the case of thin films of PP, the ductile to brittle transition is so sharp that even a test on unnotched specimen is able to detect this transition and to determine the critical molar mass.

To deal with more realistic conditions, we propose to analyse the effect of oxidation on bulk specimens of an epoxy resin exhibiting gradient of oxidation in a superficial layer. To increase the effect of the superficial layer on the mechanical response of the specimen, we propose to conduct 4 point bending tests and to measure strain to failure for different ageing conditions.

In a first part, we will present the studied epoxy resin and the thermal ageing conditions. Then, variation of elastic properties and thickness of the oxidised layer will be measured by UMI tests. Finally, we will present first results of 4 points bending tests conducted on virgin and aged specimens.

2. Material and thermal ageing

The resin on which we focus here is the CYCOM © PR520 RTM resin. It is a one-part, 180°C curing epoxy phenolic / CAF amine resin system offering good strain to failure required for composite primary structure applications. The young modulus identified at 20°C is about 4 GPa and fracture toughness is about 2.2 $MPa.m^{-1/2}$ [12].

In order to study the changes in mechanical properties induced by the thermo-oxidation of the epoxy resin, various isothermal ageing have been done on neat resin parallelepiped samples of dimensions $80x10x3mm^3$. Isothermal ageing were realized at 120°C in thermal chambers where gaseous atmosphere and pressure are controlled. Two kinds of gaseous environments, were selected: air at atmospheric pressure and pure oxygen at 3 bar in order to *accelerate* the oxidation phenomena [4,13]. Different durations of isothermal ageing tests were chosen: 500h and 1000h in air, 100h, 200h and 400h in 3 bar oxygen.

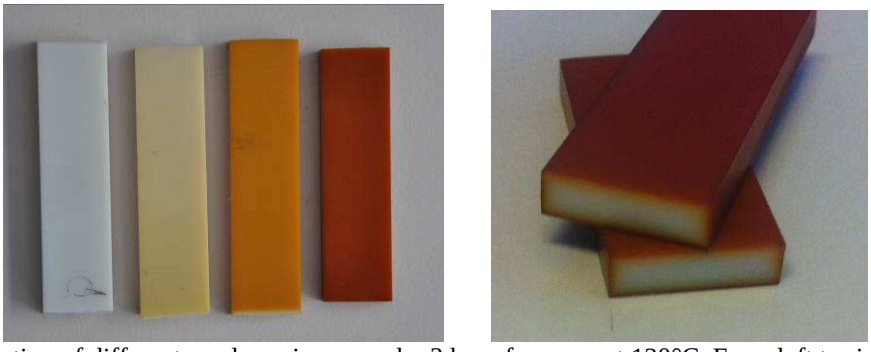

Figure 1. Coloration of different aged specimens under 3 bar of oxygen at 120°C. From left to right : Virgin, 100h, 200h, and 400h. Cut specimen showing gradient of coloration in the thickness.

The oxidation under air or oxygen leads to browning of the samples (see figure 1). This color change is more and more visible with the ageing duration and increases with oxygen pressure. According to Verdu [14], these modifications in the visible spectrum can be attributed to the oxidation of the adjuvants, in particular amines or phenols. Moreover, by looking to the transverse section of a cutted specimen, we observe the progressive coloration of the material from the virgin core to the outside surface layer.
The microstructural changes in the superficial layer of the material also affect the local elastic properties. UMI tests conducted on the transverse section of cut specimens reveal the gradient of Elastic Indentation Modulus (EIT) from the surface to the core of the specimen. Ho *et al.* [15,16] have established, for another epoxy resin, that the spatial and temporal evolution of EIT modulus can be linked to a single parameter characterizing the oxidation level.
Table 1 gathers the elastic mechanical properties of the surface layer for each sample. One can observe a local increase of the EIT modulus with ageing time. Moreover, comparison of EIT modulus obtained after ageing in air or pressurized oxygen suggests an increase of oxidation with 3 bar oxygen pressure, giving a way to accelerate thermal ageing tests. Furthermore, we can suppose that stiffening of the material will increase the stress in the oxidized layer and will promote the fracture during mechanical tests on bulk specimens.
By measuring EIT modulus from the surface to the core of the cut specimens, one can measure the depth of the oxidized layer. Results reported in table 1 show an oxidized layer that can achieve 600 µm for 400h 3b O_2 thermal ageing. In this case, oxidized layers represent one third of the total 3 mm thickness of a flexural specimen.

	Reference Virgin	1b Air 500h	1b Air 1000h	3b O2 100h	3b O2 200h	3b O2 400h
Elastic Indentation Modulus (MPa)	4.44	4.73	4.88	4.69	4.95	5.60
Oxidized thickness (µm)	0	300	400	400	500	600

Table 1. Elastic Indentation Modulus measured at the surface of the resin specimens after ageing at 120°C under different oxidative conditions and corresponding thicknesses of the oxidized layers.

3. Four points bending tests

In order to compare the strength of thick resin sample after thermal ageing, we propose to conduct 4 point bending tests on rectangular 3mm x 10mm x 80mm samples. This test produces a strain gradient in the specimen thickness, and as the oxidation leads up to several hundred micrometers thickness layer from the surface, it maximizes the strain in the oxidized layer. More over, we have shown, thanks to UMI tests that the local elastic modulus is increased by oxidation, and then it maximizes the stress in this zone. The tests were conducted on an electro-mechanical testing machine on which we have adapted a bending test device (see figure 2). The bottom roller supports are fixed on the testing frame, and the vertical displacement of the top rollers is controlled by the top grip of the testing machine. The distance between outside rollers is 50 mm and between inside rollers is 17 mm, respecting the ratio given by ASTM D6272-10 standard. The diameter of the cylindrical rollers is 10 mm. All the tests were conducted until failure with a constant displacement rate of 0.22 $mm.min^{-1}$ at room temperature 20°C.

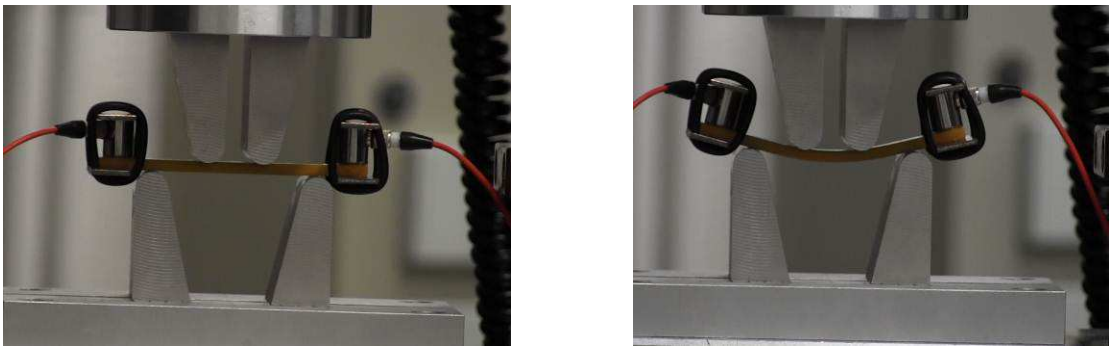

Figure 2. 4 point bending test : 200h 3 bar 0_2 oxidized specimen at the beginning of the test (left) and just before the final fracture (right).

Four point bending test force/displacement curves are reported on figure 3. Each test has been conducted twice, and the responses were reproducible. As the sections of the specimens vary slightly from one to one, each force response has been normalized by the mean section of the specimens. After correction, we observe very similar initial elastic response for the different specimens, suggesting that there is a weak influence of the oxidized layer on the overall stiffness of the specimen. However, we observe a strong influence of thermal ageing conditions on final fracture force/displacement. As the ageing duration increases, the strength of the specimen decreases. For specimens aged during 400 hours under 3 bar of oxygen pressure, final fracture vertical displacement is near a quarter of the one of unexposed specimens. We can also compare the influence of ageing under air condition (1 bar) and 3 bar of pure oxygen. The fracture displacement for 200h thermal ageing under 3 bar O_2 is comparable to the 500h one under 1 bar air. As for indentation curves, oxygen pressure seems to accelerate the effect of oxidation on mechanical properties.

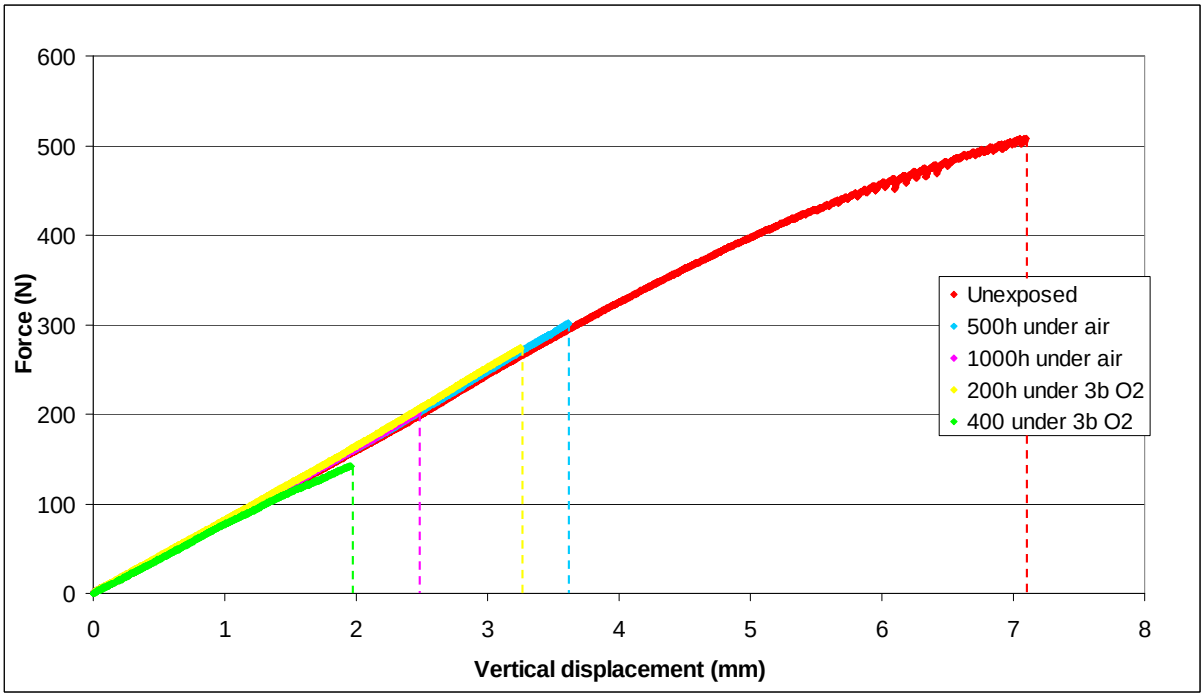

Figure 4. Four points bending test Force/Displacement curves until failure for different thermal ageing conditions.

To complete this analysis, observations by electronic microscopy show an evolution of the roughness of the fracture surfaces with ageing time (see figure 5). As the virgin and low oxidized specimens exhibit a ductile fracture surface, more aged specimens lead to more brittle fractures. We observe a ductile to brittle transition that is progressive from low to more oxidized specimens. As reported by Verdu in [14], two parameters lead to the propagation of a brittle fracture in the whole specimen: an embrittlement of the resin in surface and a critical thickness of the oxidized layer. This last one plays the role of an equivalent crack for which the length would be equal to its thickness. Finally, the progressive evolution of fracture with ageing time confirms the possibility to use this test to identify the evolution of fracture properties during thermal ageing.

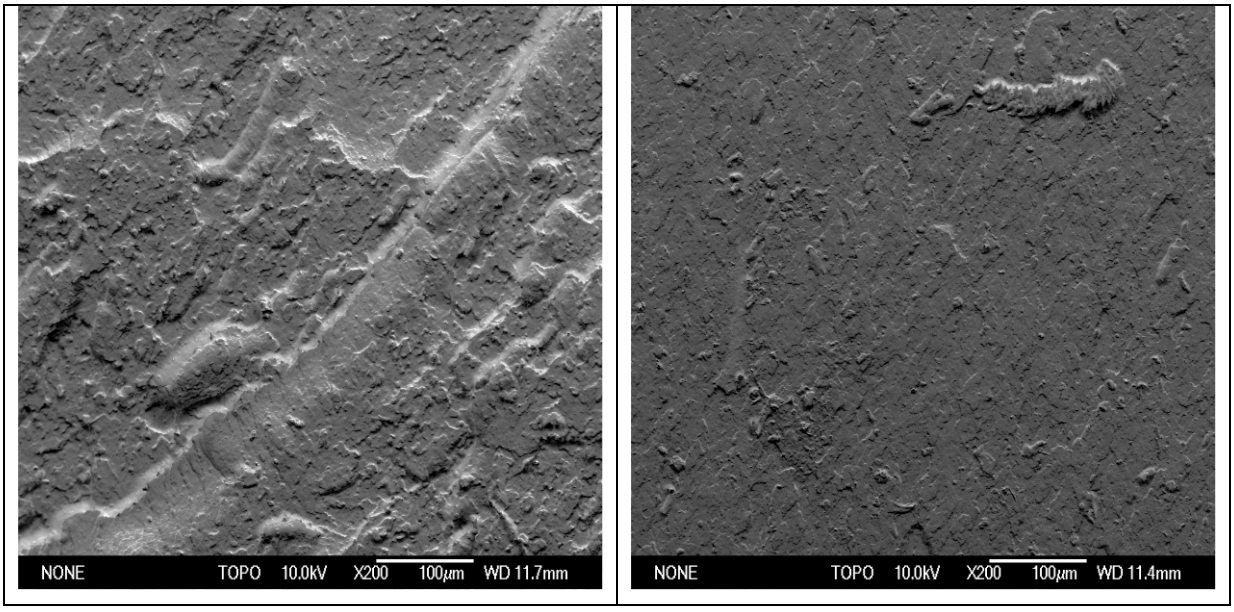

Figure 5. Fracture micrography in the bulk zone of a virgin specimen (left) and of a 400h under 3b O_2 aged specimen (right).

4. Conclusion and perspectives

The evolutions of mechanical properties of an epoxy resin after thermal ageing has been studied by UMI tests and four point bending tests. Thermal ageing leads to oxidation of the superficial layers of the bulk specimens visible by a coloration of the specimen surfaces. UMI tests reveal an increase of elastic properties from the core of the specimen to the surface layer. The thickness of the modified layer has been evaluated and its evolution for different ageing conditions has been compared.

Despite the relatively small thickness of the oxidized layer and the gradient of oxidation, four point bending tests allow us to observe a progressive influence of oxidation on strain to failure. This test seems promising to identify the influence of thermo-oxidation on strength properties of epoxy resins and to identify the ductile to brittle transtion. More instrumented tests coupled with advanced numerical models will lead to deeper analysis of this test.

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