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Material properties

# Effect of thermo-oxidation on the failure properties of an epoxy resin

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ABSTRACT

This experimental work aims at characterizing the effect of thermo-oxidation on the failure properties of a thermoset polymer used as matrix in an aeronautical composite for applications at intermediate temperatures. PR520 resin specimens were aged at 120 °C under different oxidative conditions. Thermo-oxidation leads to the occurrence of a surface layer, in which a gradient of mechanical properties (stiffness, strength, toughness …) can be measured. A multi instrumented 4-point bending test was used to evaluate the decrease of the polymer failure stress as a function of its oxidation state. According to the oxidation conditions, the embrittlement of the resin results either in an abrupt failure of the sample or in multicracking of the oxidized layer, quantified by means of strain measures and acoustic emission technique. A methodology is proposed in order to analyse the experimental data taking into account the gradient of elastic properties and residual stresses present in the oxidized layer of the specimen. In this way, the failure stress of the oxidized material is determined as function of the oxidation conditions: ageing time and oxygen partial pressure.



## 1. Introduction

In the aeronautical field, the use of carbon/epoxy composites tends to be extended to “intermediate temperatures”, close to the glass transition temperature of the polymer matrix. Among the problems linked to the employment of these materials at such temperatures, there is the need to characterize and predict the effects of thermo-oxidation of the polymer matrix on the mechanical behaviour of the material so that structural failures can be prevented.

Many research works have been dedicated to the study of thermal ageing of polymers [1], showing that thermo-oxidation of epoxy resins is due to oxygen diffusion and chemical reaction within the material, which generally depend on the exposure duration, the temperature and the oxygen partial pressure of the gaseous environment. Thermo-oxidation of polymer bulk specimens leads to a colour change and to the formation of a heterogeneous oxidized layer on the external surfaces [2,3]. In this layer, competition takes place between the oxygen diffusion and the oxygen consumption by the oxidation reaction. Using optical microscopy to observe the polished transversal section of an aged specimen, it is possible to measure, to some extent, the thickness of this layer. Many research teams modelled the thickness evolution of the oxidized layer as a function of the ageing conditions, either with semi-empirical methods [2] or with chemical kinetics approaches [3,4]. For the latter, the identification of the main kinetics constants of diffusion and reaction processes is established from gravimetric curves obtained with thin films, supposed uniformly oxidized, and with permeability and solubility measures. Until now, knowledge of the physical-chemical mechanisms responsible for the thermo-oxidation does not allow evaluating the mechanical behaviour of the oxidized material. For such evaluation, standard mechanical tests cannot be used, in particular because the oxidized layers present a gradient of mechanical properties. It can be noted that the same difficulties can be encountered in the case of non-uniform moisture content [5]. To solve this difficulty, some authors [6] suggest performing the mechanical tests on thin films, supposed to be homogeneously oxidized. However, these kinds of tests are difficult to interpret and lead to a high scatter on the failure values.

Another approach consists in determining the mechanical properties in the oxidized layer of a bulk specimen; which needs local measures and/or a gradient model. With this aim, Olivier et al. [7] have quantified the variations of the indentation elastic moduli in the oxidized layer of epoxy resins by ultra-micro-indentation

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tests. They have shown that the thermo-oxidation leads to an increase in elastic modulus at room temperature, according to the 'anti-plasticization' phenomenon previously described [8]: the occurrence of chain scissions due to oxidation causes a decrease in the glass transition temperature and in local mobility (characterized by the transition β), and thus gives rise to an increase in the elastic modulus in the domain ranged between the main ($T_\alpha$) and the secondary ($T_\beta$) transition temperatures. Furthermore, this kind of instrumented micro-indentation test, combined with following the indent recovery by interferometric confocal microscopy, made possible the modelling of the visco-elastic behaviour of the oxidized material [9].

Also, the oxidation reaction leads to a density variation of the polymer (due to oxygen atoms grafting along the polymer chain) and to a mass variation (chain scissions near the chain extremities generate a high amount of volatile products leading ultimately to a mass loss) and so to a volume reduction (chemical shrinkage). In the oxidized layer of a thick polymer specimen, in which a gradient of oxidation exists, the local density and mass changes induce a residual strain field, which promotes the matrix shrinkage observed on the surface of an oxidized composite [10]. These chemical strains, prevented by the non-oxidized core of the specimen, result in a more or less substantial residual stress field that can be responsible for spontaneous cracking at the free surface of the samples [11].

Furthermore, many studies have demonstrated that thermo-oxidation results in embrittlement of thermoset polymers [12] that involves a decrease of their strain at failure. This embrittlement is even more important when the ageing time is long and the oxygen partial pressure is high [13]. In a thick specimen, the embrittlement of the oxidized layer, associated with residual chemical strains, can promote, during ageing, spontaneous multi-cracking of the surface that can weaken the whole specimen [14]. In the context of oxidising thermomechanical loading of C/epoxy composite laminates, some attempts have been done to identify the matrix toughness reduction with oxidation level through a micro-damage model [15,16].

In that context, the identification of the properties at failure of oxidized thermoset polymers hits many difficulties. On one side, due to their brittleness, the use of thin films leads to highly scattered results. On the other side, due to the presence of a gradient of properties in an oxidized thick polymer sample, the results obtained with such specimens need to be carefully analysed. Tsuji & al. [17] proposed a set of experiments to separate some physical and mechanical properties of the oxidized surface layer from those of the unoxidised inner material, but with the assumption that the surface layer has uniform properties throughout the layer.

Following previous research work [7], in this paper, we propose to take into account the gradient of elastic properties present in the oxidized layer. Moreover, we propose a methodology that allows evaluating the influence of oxidation on the failure stress of epoxy resins. This methodology will be presented in a first part. It consists of four-point-bending tests, multi-instrumented, and performed on oxidized resin specimens. From the measures of the thickness of oxidized layers, elastic indentation modulus gradients and assessment of the chemical strains induced by oxidation, analytical calculations are developed to estimate the failure stress of the oxidized material. In a second part, the results obtained on an epoxy resin, for different ageing conditions, will be presented and discussed.

## 2. Material and characterization techniques

The studied material (Cycom PR520) is an epoxy-type thermoset polymer, with a glass transition temperature equal to 160 °C. Safran-Snecma company has provided plates from which the specimens have been cut according to the geometry prescribed for a standard 4-point bending test (L = 120 mm, b = 10 mm, h = 3.5 mm). Complete curing of the specimens has been checked through DSC analysis.

### 2.1. Thermal ageing and characterization of the oxidized layers

The specimens were aged in an isothermal environment, at 120 °C, under different gaseous atmospheres: neutral or oxidizing, and for different durations (Table 1). First, as illustrated in Fig. 1, a colour change of the samples aged in an oxidizing atmosphere can be noticed, more important for longer ageing. Moreover, it can be observed that the colour of specimens aged 1000 h in air and 200 h at 3bar of $O_2$ are similar, such as the samples aged 2000 h in air and 400 h at 3bar of $O_2$. Buch et al. have shown that the change in colour is due to chemical modifications linked to thermal oxidation phenomena [18].

The change in elastic-mechanical properties of the resin due to thermo-oxidation was characterized by Ultra-Micro-Indentation tests (UMI), by employing a Fisherscope HC100 instrumented device, equipped with a pyramidal Vickers indenter (Test conditions – max force: 5 mN, duration of the loading phase: 20 s, duration of the unloading phase: 20 s). In these tests, the indentation elastic modulus (EIT) evolution was followed along the thickness of the specimen, from the surface exposed to the environment towards the sample core. In order to obtain repeatable measures as close as possible to the surface in contact with environment, perfect flatness of the indentation surface and, therefore, a rigorous procedure for the sample preparation is needed. To do that, samples have been cut, coated and then polished to 1 μm, according to the protocol set up by Ho [19] and described in Fig. 2a. A light yellow external zone can be observed in Fig. 2b that is the oxidized layer, and the white inner part is as the virgin material.

In Fig. 3, the results of UMI tests performed on aged specimens are presented. Elastic indentation modulus (EIT) values have been normalized compared to that of the virgin material. An 'oxidation tracer gamma', γ, has been defined as:

$$\gamma = \frac{EIT_{measured}}{EIT_{virgin}} - 1$$

The mean value of $EIT_{virgin}$ for the non-oxidized resin has been evaluated from 140 measures, and each point of the graphic in Fig. 3 tallies with the average value of a twelve-measure series. These twelve measures have been realised at the same distance from the external surface in contact with the ageing environment. To better understand the figure, the error associated with the average values is not represented on the diagram. However, the standard deviation, evaluated through statistical analysis, is less than 1%.

In Table 2, the characteristics of the oxidized layers for the considered ageing conditions are summarised. In order to avoid the bias due to the proximity of the indenter with the edge of the specimen, the indentation module variation, EIT(%), is the value of the parameter γ measured at a distance from the external surface of 30 μm, and the oxidized layer depth is defined as the zone size for which γ values are higher than 1%. We can note great uncertainty

**Table 1**
Ageing conditions for PR 520 samples.

| Environment | Pressure (bars) | Duration (hours) | Temperature (°C) |
|---|---|---|---|
| Nitrogen ($N_2$) | 3 | 200 | 120 |
| Air | 1 | 500/1000/2000 | 120 |
| Oxygen ($O_2$) | 3 | 100/200/400/600 | 120 |