

## IMPACT OF TEMPERATURE AND THERMAL CYCLING AGEING ON PERFORMANCE OF 3D WOVEN COMPOSITES WITH POLYMER MATRIX MANUFACTURED BY RTM

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### Abstract

*This work aims to a better understanding of damage mechanisms in carbon/epoxy 3D woven composites submitted to thermal cycles. Isothermal ageing highlighted the impact of thermo-oxidation on the elastic properties of the matrix. Besides, thermal cycling ageing performed in neutral (nitrogen) and oxidative (air and oxygen) atmospheres revealed the initiation of microcracks in the matrix due to thermal cyclic stresses.*

*An advanced study of the composite microcracking, which early results are presented here, using both 2D (optical microscopy) and 3D (X-Ray tomography) observations is in progress in order to determine the effect of the fibres architecture and the impact of the ageing environment on the path and depth of microcracks.*

### 1. Introduction

As part of the development of lighter and long-lasting aircraft structures, it is considered to introduce some parts made of 3D woven composites with polymer matrix, manufactured by RTM (Resin Transfer Molding) process. In this kind of applications, possible interest of 3D composite materials comes from their better damage tolerance than composite laminates [1]. In this work, a 3D composite made of a ply to ply interlock fabric preform is studied. For this material, studies have already been lead to characterize both low-velocity and high-velocity impact behaviors [2, 3], and to identify their damage mechanisms under static [4] and cyclic [5] mechanical loadings. Results of these experimental studies were associated to modeling activities in order to develop tools for service life predictions [6-7]. However, the lifetime prediction of structures in service requires to take into account the effects of temperature, and particularly of *thermal cycles*, on the damage mechanisms, since it has been demonstrated they have a significant impact on matrix cracking in organic matrix composite laminates.

Throughout the 1990s and early 2000s, several teams have studied the damage mechanisms of composite laminates, made of polymer matrix and reinforced with continuous carbon fibers, subjected to "aeronautical" thermal cycles [8-11]. These works were mainly linked to projects for the development of supersonic aircrafts. In this kind of applications, the constituent materials of the aircraft structural parts are subjected to cyclic mechanical loadings as well as great amplitude temperature variations depending on the phase of flight: subsonic or supersonic. These variations of temperatures, repeated for each flight, can be the origin of a thermo-mechanical fatigue, one flight corresponding to one thermal cycle. Besides, high

temperature exposure (even below the glass transition temperature of the matrix) can lead to the ageing of the polymer matrix, particularly due to its oxidation. Some authors have shown, thanks to isothermal ageing in oxidative environment that the oxidation of an epoxy matrix results in superficial damage affecting only the “skin” of the samples [12]. The oxidation phenomenon comes with a loss of mass, an increase in density and a degradation of the mechanical properties [13]. In case of isothermal ageing of thick samples, oxidation is considered as the main factor for cracks initiation at the specimen surface, when the local stress exceeds the ultimate strength of the oxidized matrix [14]. In case of a unidirectional composite, the matrix oxidation creates matrix shrinkage contributing to early debonding between fibres and matrix [15-17]. Advanced studies were undertaken to understand and model the chemo-thermo-mechanical coupling present in the thermal oxidation of an epoxy matrix composite [18]. These authors also highlighted the possibility to accelerate the thermal oxidation processes by using pressured oxygen atmosphere. Besides, thermal cycling tests of composite laminates in oxidative environment have shown that the presence of intralaminar cyclic mechanical stresses accelerates the matrix cracks initiation at the edges in contact with the environment and drives them from the edge to the core of the samples [15].

More recently, studies [19] regarding aerospace applications have been realized with thermal cycles (-175°C/120°C) under vacuum, and a very recent study on 3D braided carbon epoxy composites subjected to cyclic thermal loading (-55°C/120°C) in air, has shown that the nature of the matrix controls the composites sensibility to cracking [20].

This bibliographic review shows that, in the case of carbon/epoxy composites exposed to thermal cycles, there exists a coupling of thermal, chemical and mechanical phenomena in the cracking mechanisms. Even though some of the damage mechanisms observed on composite laminates could probably be applied to 3D woven composites, the originality of this study lies in the architecture complexity of ply to ply interlock materials and in the effects of a gaseous environment. Indeed, in order to separate the thermal, chemical and mechanical phenomena that all interact during a long term thermal cycling of a 3D woven carbon/epoxy composite, the proposed approach is to perform tests either in neutral or oxidative atmospheres i/ to study the isothermal ageing of the epoxy matrix, and ii/ to analyse composite damage induced by thermal cycling. In order to compare our results to those of Zhang *et al.* [20], we have imposed the same amplitude of thermal cycles, (-55°C/120°C), which is a generic cycle in ageing studies.

Results presented here are the first data of a work in progress aiming to a better understanding of the damage mechanisms in stake in carbon/epoxy<sup>1</sup> 3D woven composites submitted to thermal cycles. In the following, impact of thermo-oxidation on the elastic mechanical properties of the epoxy matrix is studied using ultra-micro-indentation tests. In a second part, the methodology used for observing microcracks in 3D composite samples is presented as well as first results on microcracking generated by thermal cycling in different atmospheres.

## 2. Thermo-oxidation of the epoxy resin

### 2.1. Preparation and ageing of the samples

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 60x10x3mm<sup>3</sup>. These samples were previously dried under vacuum at 70°C.

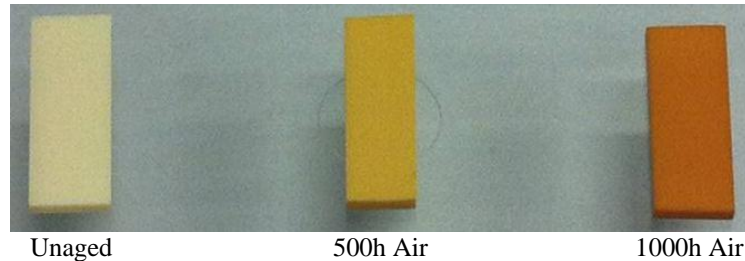
Isothermal ageing were realized at 120°C in thermal chambers where gaseous atmosphere and pressure are controlled. Three kinds of gaseous environments, at atmospheric pressure, were selected: air (atmospheric pressure: 0,1 MPa as in [20]), pure oxygen (O<sub>2</sub>) at 0.3 MPa in order

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<sup>1</sup> Commercial name of the resin won't be given due to confidential matters.

to *accelerate* the oxidation phenomena [17-18, 21] and pure *neutral* nitrogen atmosphere (N<sub>2</sub>) at 0.3 MPa. Different durations of isothermal ageing tests were chosen: 500h and 1000h in air, 100h 200h and 400h in (O<sub>2</sub>), 200h in (N<sub>2</sub>)

As an example, Figure 1 shows the appearance of a virgin epoxy resin sample and two aged specimens exposed to air atmosphere during respectively 500h and 1000h.



**Figure 1.** Surface appearance of one virgin sample and two oxidized samples

In this figure, one can observe a change in color for the oxidized samples. This change is more and more visible with the ageing duration. Ageing under pressure of oxygen lead to similar changes in color but for shorter ageing times. It was also checked that an ageing in N<sub>2</sub> (as in vacuum) didn't lead to any visual change in color. According to Buch *et al.* [22], these modifications obtained under oxidative atmospheres indicate chemical modifications due to thermo-oxidation.

During the 120°C isothermal ageing tests, the samples weight was followed to get information on the oxidation kinetics for this specific resin. These tests show a continuous increase in weight for the samples aged in air and in oxygen. This increase is faster as the pressure and the concentration of oxygen are higher. Moreover, no variation in weight was observed for the sample aged in nitrogen. These results suggest that for the epoxy resin under study and with these experimental conditions, the oxygen diffusion processes are faster than the ones of formation of oxidation products.

## 2.2. Characterization of the oxidized layer by Ultra-Micro-Indentation technique

Variations in the resin elastic mechanical properties induced by thermo-oxidation are studied by means of Ultra-Micro-Indentation tests (UMI). This technique allows following the evolution of the elastic indentation modulus (EIT) in the sample thickness, starting from the surface exposed to the oxidative environment. These measurements are used to identify the thickness of the oxidized layer as well as the intensity of the gradient of elastic properties. Besides, Ho *et al.* [23-24] 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.

In order to realize UMI tests, samples were cut, coated and polished according to the protocol described by Ho *et al.* [23-24]. The EIT modulus of the dry virgin resin was obtained from 140 measurements, presented in Figure 2 by a hatched area corresponding to the standard deviation of those measures. In this figure, EIT modulus values are normalized with respect to that of the virgin resin. Each point corresponds to the mean value of twelve measurements realized at the same depth from the surface in contact with the ageing atmosphere. Measurement uncertainty is estimated to be lower than 1% by statistical analysis.

Table 1 gathers the elastic mechanical properties of the oxidized layer for each sample. Variation in EIT modulus is defined as the difference between the normalized values at 30 µm and at 1000 µm from the sample surface - the later being found equal to the EIT modulus of

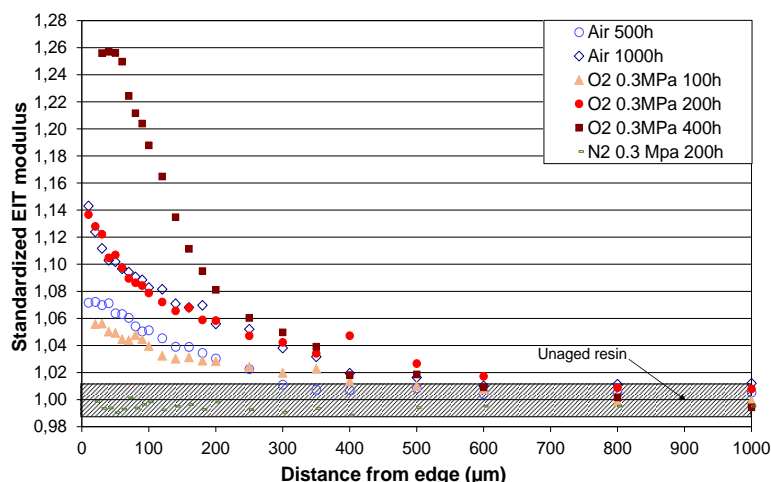
the unaged material. In the same manner, the depth of the oxidized layer is defined as the distance until which this variation is higher than 1%.

First of all, it can be noticed in Figure 2 that the thermal ageing under 0.3 MPa pressure of N<sub>2</sub> during 200h does not lead to any noticeable variation of the elastic modulus: indeed, values obtained either on the edge or in the center of that sample are included in the dispersion range of the initial EIT modulus of the virgin resin. However, after an isothermal ageing under oxidative environment, one can observe a more or less important gradient of properties in a superficial layer (defined as the oxidized layer), in which the EIT modulus decreases from the surface to the core of the specimen, where the initial value is found.

Increases in EIT modulus of the oxidized layer of samples aged during 500h and 1000h in air vary from 6% to 10% whereas the increases for samples aged under 0.3MPa pressure of O<sub>2</sub> during 100h, 200h, and 400h vary from 6% and up to 26% (Table 1).

Depths of the oxidized layer of samples aged during 500h and 1000h in air vary from 300 μm to 400 μm whereas depths for samples aged under 0.3MPa pressure of O<sub>2</sub> during 100h, 200h, and 400h vary from 400 μm to 600 μm (Table 1).

For given conditions of temperature and oxidative atmospheres, variation in EIT modulus and depth of the oxidized layer are thus higher as the ageing time is longer. Moreover, these increases are even higher if ageing are realized under oxygen pressure.



**Figure 2.** Evolutions of EIT modulus in the thickness of resin samples aged 500h and 1000h in air, 100h, 200h and 400h under 0.3MPa pressure of O<sub>2</sub> and 200h under 0.3MPa pressure of N<sub>2</sub> at 120°C

Properties	Ageing					
	Air 500h	Air 1000h	O2 0,3 MPa 100h	O2 0,3 MPa 200h	O2 0,3 MPa 400h	N2 0,3 MPa 200h
EIT Variation (%)	6,4	9,8	5,7	11,3	26,3	0
Depth of oxidized layer (μm)	300	400	400	500	600	0

**Table 1.** Variation of EIT modulus and depths of oxidized layers of various resin samples aged at 120°C under neutral (N<sub>2</sub>) and oxidative atmospheres (Air and O<sub>2</sub>)

Figure 2 also shows that the evolutions of EIT modulus of samples aged during 500h in air and during 100h under 0.3MPa pressure of O<sub>2</sub> are similar. The same conclusion can be made by comparing the evolution of EIT modulus of samples aged during 1000h in air and during 200h under 0.3MPa pressure of O<sub>2</sub>. For these ageing conditions, results suggest that using a 0.3MPa pressure of oxygen accelerates by five times the ageing time.

A resin specimen was also exposed to thermal cycles between -55°C and 120°C for an aging time of approximately 1000h in oxidative environment: UMI measures show the presence of a thin oxidized layer associated to a very weak increase in EIT modulus (close to the dispersion range of the EIT value of the virgin resin).

### 3. Thermal cycling ageing of composite samples

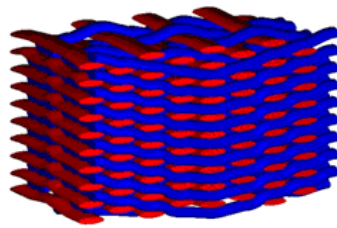
To separate the thermal, chemical and mechanical phenomena that all interact during a long term thermal cycling of a carbon/epoxy composite, tests in neutral and oxidative atmospheres are used. First work was to set a thermal cycling testing device whose atmosphere and temperature are fully controlled. Secondly, work focused on damage observation techniques and damage analysis in order to compare effects of different gaseous atmosphere.

When composite materials with long continuous fibers are subjected to thermal cycles, the mismatch of thermal expansion coefficients of fibers and matrix induces local variations of mechanical stresses at the constituents scale, especially higher at lower temperatures.

On the other hand, oxidation of the matrix occurring at the composite surface at the highest temperatures of the thermal cycle can generate local stresses due to alterations in the mechanical properties of the resin. Following a similar protocol to that used above for studying the isothermal aging of the epoxy resin, numerous thermal cycling tests were performed using different gaseous atmospheres (air, O<sub>2</sub>, N<sub>2</sub>), in order to separate the thermo-mechanical contributions from the chemical ones. Composite samples were then analyzed using both 2D (optical microscopy) and 3D (X-Ray tomography) techniques.

#### 3.1. Preparation of composite samples

Three-dimensional woven preforms can be classified in different categories but they are all gathered in the generic term of multi-layer interlock fabrics [25]. The composite materials of this study has an angle interlock pattern called « Ply-to-ply Angle Interlock ». In this pattern, the warp columns are interlaced and only go through some weft layers as shown in Figure 3.



**Figure 3.** Ply-to-ply interlock pattern example [<http://www.mtm.kuleuven.be/>]

In this study, plates made of carbon epoxy interlock composite were manufactured by RTM process by SNECMA. In these plates, samples were taken whose dimensions correspond to one complete mesh of the periodic interlock pattern in order to estimate the impact of the fabric geometry on the damage mechanisms.

Besides, machined surfaces were polished until mirror aspect in order to erase all cutting defects and enable optical follow-up during the ageing.

#### 3.2. Experimental device of thermal cycling test

In this work, thermal cycles were imposed using a SECASI-SERVATIN thermal cycling chamber, in which a smaller environmental chamber was added in order to control the gaseous atmosphere. This experimental device was developed in the PhD work of S. Rouquié [26]. In the environmental chamber, a constant flow of gas is applied with a small overpressure of 20mbar. Various gaseous mixtures of different oxygen concentrations can be obtained from industrial dry gases.

The thermal cycling test was set up between - 55°C and 120°C at a rate of 5°C/min. The highest temperature is about 50°C lower than the glass transition temperature of the resin.

This range of temperatures was chosen identical to the ones in Zhang's work [20], in order to be able to compare results. Temperature is controlled using a thermocouple placed inside the environment chamber.

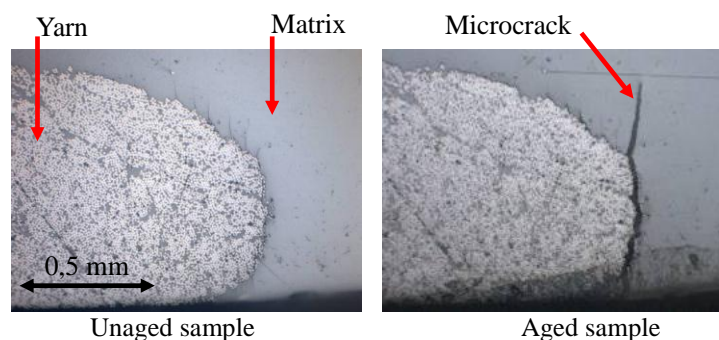
During thermal cycling test, temperatures were checked on the samples surfaces with a heat image camera and with a thermocouple placed in the center of a specimen. The difference in temperatures between the sample core and the sample surface was about 8°C.

A finite element calculation was also performed on the composite sample geometry in order to evaluate the theoretical temperature gradient through the sample thickness during the thermal cycling test. The features of this preliminary simple calculus are the following: the mechanical behavior of the carbon fiber yarns and the epoxy matrix are considered as linear elastic; the yarns thermal properties are estimated according to the volumetric proportions of polymer matrix and carbon fibers; the thermal loading was applied by setting the temperature at the sample surface nodes. The results of this calculation give a maximal temperature gradient between the surface and the core of the sample of approximately 1.5°C, allowing us to consider that temperature gradients in the composite samples can be ignored. This hypothesis seems reasonable given the low heating and cooling rates applied and the high thermal conductivity of carbon fibers yarns.

### 3.3. Microcracking initiation

Several thermal cycling tests were performed in air, O<sub>2</sub> and N<sub>2</sub> atmospheres. The tests were stopped at regular intervals in order to observe the polished surfaces of the specimens. Microscopic observations allowed to observe the location of the first cracks and to follow their propagation all along the ageing time.

Figure 4 gives an example of a first microcrack visualized on the surface of the sample, in the warp direction, during a thermal cycling test in *nitrogen* atmosphere. This figure shows that the first microcracks initiate preferentially at the fiber/matrix interface. It also highlights the fact that, in this material, the mismatch of thermal expansion coefficients of fibers and matrix can generate local mechanical stresses high enough to initiate matrix microcracking, without any chemical contribution of thermo-oxidation, since it occurs in a neutral environment. Moreover, such microcracks have been observed both in the warp and weft directions



**Figure 4.** Zoom surface micrography of a sample exposed to thermal cycles in N<sub>2</sub> atmosphere

Similar observations have been made on samples exposed to thermal cycles in oxidative atmospheres (air and O<sub>2</sub>).

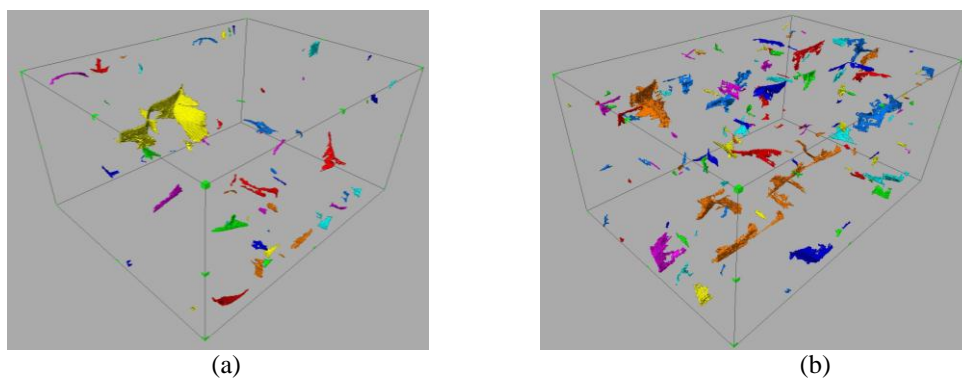
The fibrous three-dimensional architecture of these samples make very complex the analysis and understanding of the cracking mechanisms. In order to investigate the impact of the 3D pattern in cracking paths as well as the effects of thermo-oxidation in the generated cracks size, and especially their depth, 2D analysis realized by optical microscopy need to be completed with 3D observations techniques as X-ray microtomography.

In the case of this study concerning the onset and propagation of very thin and short cracks, 3D observations require really high-resolution images. 3D scans of the aged samples were therefore realized by synchrotron X-ray microtomography at ESRF Grenoble in France.

Volume inspections were done for samples aged in air, O<sub>2</sub> and N<sub>2</sub> atmospheres from the 3D reconstructions, thanks to image processing and segmentation techniques.

The microcracks present in samples exposed to numerous thermal cycles in N<sub>2</sub> and O<sub>2</sub> atmospheres are given as examples in figure 5.

In this figure, only the microcracks present in the samples are represented, without resin nor carbon fiber yarns. Moreover, each independent defect is represented with a different color. A comprehensive analysis of these pictures shows that microcracking concern only the polymer matrix (no fiber breakage is observed), and that microcracks are mainly located in pockets of resin or at the resin/yarn interface. When they encounter a fiber strand, they propagate locally in the strand matrix and along the fibers. Only very few and small microcracks were observed in the center of the specimens with no connection to any surfaces.



**Figure 5.** Comparison of microcracking in samples exposed to thermal cycles (a) in N<sub>2</sub> (b) in O<sub>2</sub> atmosphere

These cracking mechanisms are observed both in neutral and oxidative environment. However, crack initiation seems to be accelerated in oxidative environment. Work is in progress to quantify the exact contribution of thermo-oxidation on microcracking in the studied composite, tested with these experimental conditions.

It appears that our analysis of microcracking mechanisms induced by thermal cycling can't be directly compared to that described in the work of Zhang *et al.* [20], because of the great difference in 3D architectures of the samples. This observation highlights the key part of the composite architecture on the damage mechanisms. However, according to microcrack densities and aging duration, our composite seems to behave like Zhang's more tenacious one. In order to confirm these preliminary observations, work is in progress to study two composites of same fibrous architecture but with two different epoxy resins: the one studied in this paper and another one known as to be fragile.

#### 4. Conclusions and perspectives

Results presented here are part of a study aiming to a better understanding of the damage mechanisms in carbon/epoxy 3D woven composites submitted to thermal cycles. Presented work highlighted the studied matrix sensitivity to thermo-oxidation at 120°C. In particular, the formation of an oxidized layer whose thickness grows as the ageing time and the oxygen pressure increase was observed. In this oxidized layer, an increase in the elastic modulus was measured by micro-indentation.

This work also shows that the mismatch of thermal expansion coefficients of fibers and matrix can generate local mechanical stresses high enough to initiate matrix microcracking during a thermal cycling (-50°C/120°C) in a N<sub>2</sub> neutral environment. Comparison between

tests performed in neutral and oxidative atmospheres showed that cracking mechanisms are similar, even though crack initiation seems to be accelerated in oxidative environment.

In future works, an advanced study of the composite microcracking from 3D tomographic data will be undertaken in order to determine the effect of the fibres architecture, the brittleness of the polymer matrix and the impact of the environment. A numerical model of the thermal cycling test will also be developed in order to have a better understanding of the observed phenomena. For numerical model needs, the temperature-dependent behaviour law of the epoxy resin will have to be identified.

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## References

- [1] A. P. Mouritz, « Three dimensional (3D) fibre reinforcements for composites ». *Composites reinforcements for optimum performance*, Woodhead Publishing, pp. 157-199, 2011.
- [2] F. Cui, B. Z. Sun, and B. H. Gu, «Fiber inclination model for finite element analysis of three-dimensional angle interlock woven composite under ballistic penetration ». *Journal of Composite Materials*, vol. 45, no. 14, pp. 1499-1509, Jul, 2011.
- [3] P. Potluri *et al.*, « Influence of Fibre Architecture on Impact Damage Tolerance in 3D Woven Composites ». *Applied Composite Materials*, vol. 19, no. 5, pp. 799-812, Oct, 2012.
- [4] J. Schneider, « Mécanismes d'endommagement dans les composites multicouches à renforts interlock ». *PhD, Université de Technologie de Compiègne*, 2011.
- [5] J. Henry *et al.*, « Fatigue damaging analysis of a carbon / epoxy 3D layer Interlock with Acoustic Emission ». *JNC17*, 2011.
- [6] L. Marcin *et al.*, « Experimental Investigation and Behavior Modeling of a 3D Interlock Woven Fabric Composite: Part 2 ». *TexComp9*, 2008.
- [7] C. Rakotoarisoa *et al.*, « Development of a fatigue model for 3D woven polymer matrix composites based on a damage model ». *ECCM15, Venice, Italy*, 2012.
- [8] G. A. Owens, and S. E. Schofield, « Thermal cycling and mechanical property assessment of carbon-fiber fabric reinforced PMR-15 polyimide laminates ». *Composites Science and Technology*, vol. 33, no. 3, pp. 177-190, 1988.
- [9] S. H. Lee *et al.*, « Thermo-oxidative stability of high performance composites under thermal cycling conditions ». *Journal of Composite Materials*, vol. 35, no. 5, pp. 433-454, 2001.
- [10] S. Ogihara, N. Takeda, and A. Kobayashi, « Effects of thermal cycling on microscopic damage progress in laminated composites ». *Fracture and Strength of Solids, Pts 1 and 2: Pt 1: Fracture Mechanics of Materials; Pt 2: Behavior of Materials and Structure*, vol. 145-9, pp. 775-780, 1998.
- [11] S. Ogihara *et al.*, « Damage mechanics characterization of transverse cracking behavior in quasi-isotropic CFRP laminates with interlaminar-toughened layers ». *International Journal of Fatigue*, vol. 24, no. 2-4, pp. 93-98, Feb-Apr, 2002.
- [12] T. K. Tsotsis *et al.*, « Aging of polymeric composite specimens for 5000 hours at elevated pressure and temperature ». *Composites Science and Technology*, vol. 61, no. 1, pp. 75-86, 2001.
- [13] X. Colin, and J. Verdu, « Strategy for studying thermal oxidation of organic matrix composites ». *Composites Science and Technology*, vol. 65, no. 3-4, pp. 411-419, Mar, 2005.
- [14] X. Colin *et al.*, « Interaction between cracking and oxidation in organic matrix composites ». *Journal of Composite Materials*, vol. 39, no. 15, pp. 1371-1389, 2005.
- [15] M. C. Lafarie-Frenot, and S. Rouquie, « Influence of oxidative environments on damage in c/epoxy laminates subjected to thermal cycling ». *Composites Science and Technology*, vol. 64, no. 10-11, pp. 1725-1735, Aug, 2004.
- [16] G. P. Tandon, and K. V. Pochiraju, « Heterogeneous Thermo-oxidative Behavior of Multidirectional Laminated Composites ». *Journal of Composite Materials*, vol. 45, no. 4, pp. 415-435, Feb, 2011.
- [17] D. Q. Vu, M. Gigliotti, and M. C. Lafarie-Frenot, « Experimental characterization of thermo-oxidation-induced shrinkage and damage in polymer-matrix composites ». *Composites Part a-Applied Science and Manufacturing*, vol. 43, no. 4, pp. 577-586, Apr, 2012.
- [18] L. Olivier *et al.*, « Development of experimental, theoretical and numerical tools for studying thermo-oxidation of CFRP composites ». *Composites Part a-Applied Science and Manufacturing*, vol. 40, no. 8, pp. 1008-1016, Aug, 2009.
- [19] S. Y. Park *et al.*, « Effect of vacuum thermal cyclic exposures on unidirectional carbon fiber/epoxy composites for low earth orbit space applications ». *Composites Part B-Engineering*, vol. 43, no. 2, pp. 726-738, Mar, 2012.
- [20] C. Zhang *et al.*, « Experimental and FEM study of thermal cycling induced microcracking in carbon/epoxy triaxial braided composites ». *Composites Part a-Applied Science and Manufacturing*, vol. 46, pp. 34-44, Mar, 2013.
- [21] X. Colin, C. Marais, and J. Verdu, « A new method for predicting the thermal oxidation of thermoset matrices - Application to an amine crosslinked epoxy ». *Polymer Testing*, vol. 20, no. 7, pp. 795-803, Oct, 2001.
- [22] X. Buch, and M. E. R. Shanahan, « Thermal and thermo-oxidative ageing of an epoxy adhesive ». *Polymer Degradation and Stability*, vol. 68, no. 3, pp. 403-411, 2000.
- [23] L. Olivier, « Prédiction du vieillissement thermo-oxydant de composites à matrice organique dédiés à l'aéronautique : Prise en compte des couplages multiphysiques ». *PhD, LMPM, ENSMA, UMR CNRS 6617, Poitiers*, 2008.
- [24] N. Q. Ho, « Endommagements de composites carbone/époxy induits par la thermo-oxydation de la matrice en présence de contraintes mécaniques ». *PhD, Université de Poitiers - ENSMA*, 2006.
- [25] F. Abdi, L. Minnetyan, and C. C. Chamis, « Fracture mechanics of metals, composites, welds, and bolted joints ». *Kluwer Academic Publishers*, Chapter 8, 2000.
- [26] S. Rouquie, « Vieillissement de structures composites à matrice organique soumises à des chargements thermomécaniques répétés ». *PhD, Université de Poitiers - ENSMA*, 2003.