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# RHEOKINETICS OF THERMOSETTING PREPREGS BEFORE GELATION: AN ORIGINAL DEVICE AND EXPERIMENTAL CHARACTERIZATION PROCEDURE

Rima Sfar Zbed<sup>1,2</sup>, Steven Le Corre<sup>2</sup>, Vincent Sobotka<sup>2</sup> and Mael Péron<sup>3</sup>

<sup>1</sup>IRT Saint-Exupéry, F-31405 Toulouse, France

Email: [rima.sfarzbed@irt-saintexupery.com](mailto:rima.sfarzbed@irt-saintexupery.com), Web Page: <https://www.irt-saintexupery.com/fr/>

<sup>2</sup>Nantes Université, CNRS, Laboratoire de thermique et énergie de Nantes, LTeN, UMR 6607, F-44000 Nantes, France, [steven.lecorre@univ-nantes.fr](mailto:steven.lecorre@univ-nantes.fr), [vincent.sobotka@univ-nantes.fr](mailto:vincent.sobotka@univ-nantes.fr), <https://lten.cnrs.fr>

<sup>3</sup>Nantes Université, École Centrale Nantes, CNRS, GeM, UMR 6183, [F-44600 Saint-Nazaire], France [mael.peron@univ-nantes.fr](mailto:mael.peron@univ-nantes.fr), <https://gem.ec-nantes.fr/>

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## Abstract

Knowledge about the mechanical properties' evolution of thermosetting composites throughout the manufacturing process is a very essential step in understanding the development of certain mechanisms, such internal stress generation and parts deformations, which are controlled by the presence of multiple multi-physics phenomena that occur during the cure. This paper presents an original experimental approach, based on the use of the PVT-HADDOC device, dedicated to analyze the mechanical behavior of a unidirectional aeronautical composite during curing, and especially before the gel point. The test was based on a lubricated compression test sequence, under constant hydrostatic pressure, with stress levels adapted to the evolution of the degree of cure. They enabled to characterize the out-of-plane compressive rheology of the composite. Results show a viscoelastic behavior that can be obtained from the liquid state up to a degree of cure of about 60%, with a Burger's type 4-parameters model.

## 1. Introduction

Identifying the mechanical behavior of thermosetting composites and understanding the evolution of the mechanical properties during the cure process is of crucial importance to predict the initial residual stresses state and optimize the composite processing parameters and defect mitigation. Most works about the development of residual stresses and their modeling have focused on the post gelation region, thus assuming that energy and stresses storage in the composite of earlier stages of the curing process have no effect. Different approaches in the literature now well established, such as the CHILE model [4] or the pseudo visco-elastic approach (PVE) [5] assume a thermoelastic model after the gel point, with a progressive increase of the anisotropic elasticity or viscoelasticity. On the other hand, the original works of [3] assumed the existence of a yield stress in the polymer matrix, linked to the gelation phenomenon and increasing with the degree of cure, which makes a transition between an elastic behavior and an inelastic (viscous) one. Above the yield stress, stresses are assumed to relax. Those works suggest in fact a more complex behavior in the so-called liquid state that can be assimilated to a semi-solid or semi liquid state in the matrix, which could lead to complex rheological evolutions in the composite during curing. Up to day, no convincing experimental approach, in industrial process representative conditions, enable to analyze properly the behavior of thermoset composite material before gelation, where most of the process induced deformations are generated. In previous works [1-2], the present group of authors presented the PVT-HADDOC device, that was proved to enable the analysis of anisotropic thermal and mechanical strains during all the curing of thermoset composites. In [2], the analysis of process induced thermal expansion and chemical shrinkages, all over the curing cycle, on the same material as studied

here led to original observations. In particular, a sharp transition of the chemical shrinkage behavior near the conventional gel-point ( $\sim 52\%$  of degree of cure). Before gelation, shrinkage would occur mainly in the thickness, whereas after gelation it would evolve towards a quasi-transversely isotropic behavior. This was the first step towards a better description of dimensional evolution during curing, based on fine experimental measurements.

Now, the objective of this work is to present an original experimental methodology, with an associated analytical model to identify the rheological properties of a unidirectional interlayer toughened aerospace prepreg during curing. After a short description of the experimental procedure using the already published PVT-Haddoc device [1-2], the specific mechanical testing in compression mode is described. The viscoelastic behavior up to about 50% of degree of cure is then identified. A simple 4 parameters viscoelastic model, identified over the whole curing cycle is then proved to fit perfectly the experiment data.

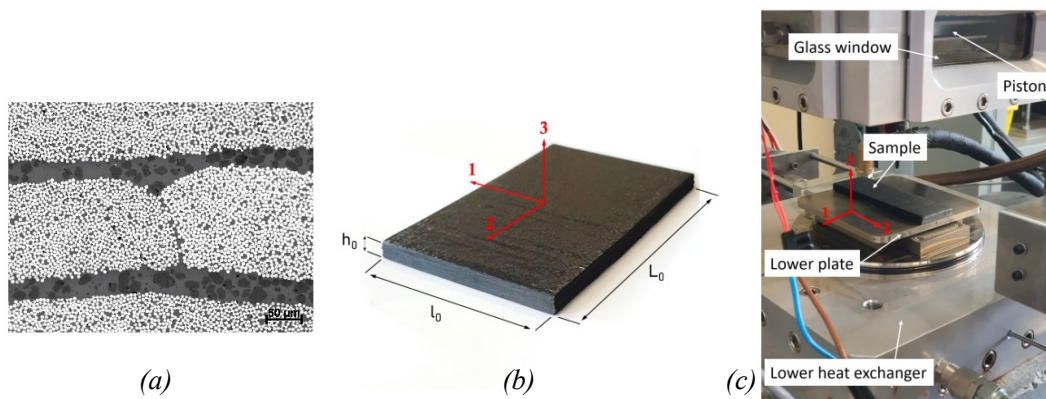
## 2. Material, experimental setup and procedure

### 2.1. Material

This study was conducted with a unidirectional aerospace-grade prepreg supplied by Hexcel Composites, HexPly® M21/34%/UD194/IMA-12K. This prepreg is made of a M21 epoxy resin and IMA carbon fibers with a nominal cured ply thickness of 0.184 mm [A]. The IMA/M21 system is a toughened prepreg that includes extra layers of resin incorporating undissolved thermoplastic particles as distinct interleaves between plies as illustrated in Figure 1(a). As shown in Figure 1(b), samples of planar dimensions  $105 \times 30 \text{ mm}^2$  were cut from unidirectional layup of 30 plies leading to a consolidated thickness of  $5.91 \pm 0.05 \text{ mm}$ .

### 2.2 Experimental setup

The PVT-HADDOC apparatus was already fully described in previous works [A,B]. It is basically a pressurized three-dimensional dilatometer which has been proved to provide accurate measurements of the anisotropic coefficients of thermal expansion (CTE) and of chemical shrinkages (CCS) for thermal and pressure cycles representative of industrial conditions. It is to notice that, conversely to conventional apparatuses, those measurements can be performed from the liquid to the solid state, all along the curing cycle. Mounted on a universal testing machine (Instron ElectroPulse E10000), the PVT-Haddoc can also be used as a linear rheometer that can analyze the behavior of composites in compression along the out-of-plane direction.



**Figure 1.** IMA/M21E composite with interleaves, optical micrograph of a cross section in the transverse direction.

## 2.3 Test protocol

As depicted in Figure 2(a), samples were submitted to a specific curing cycle, consisting in a fast heating ramp at 4K/min followed by an isothermal step of 120 min at 160°C, under a hydrostatic chamber pressure of 0.5MPa. This enables to decouple almost perfectly the heating and the curing stages. Doing so, the rheological evolutions due to the changes in the degree of cure  $\alpha$  only can be tested on the isothermal step. The PVT-HADDOC being based on the realization of a homogeneous thermal and mechanical step thanks to a thorough lubrication of both platens, only compression tests can be performed on this system. The Electropulse machine nevertheless enables to perform complex sequences of almost any type of test procedures. In order to follow at best the stiffening rheological evolution of the UD composite in the transverse direction, creep-like test with increasing values of the compression stress were applied to the sample. They are shown in Figure 2(b). The duration of the compression was intentionally limited to an arbitrary “small” value of 16s in order to avoid too much flow of the material. Tests are repeated every 100s which corresponds to roughly a spacing of 1% of  $\alpha$ . The cumulated macroscopic flow was checked to be small after the 120 minutes of testing. Applied stress levels are given in Figure 2(a), they follow some exponential evolution up to the maximum capacity of the press machine.

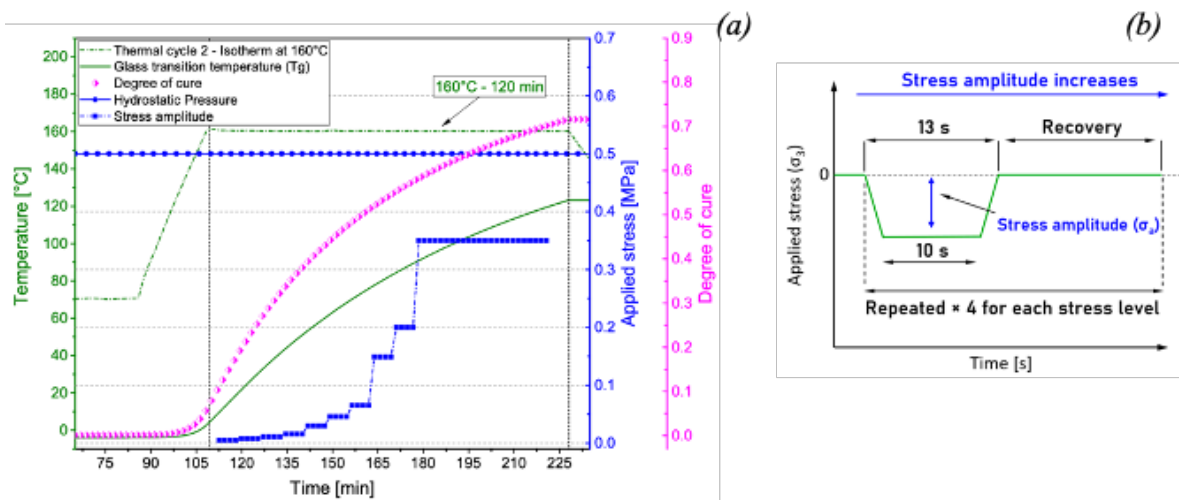
## 2.4 Strain analysis

Conversely to our prior works on the multiaxial measurements of CTEs and CSSs [A],  $\varepsilon_3$  was studied here. After a classical correction of the machine compliance, the analysis of the mechanical strain requires to remove the chemical strain that continuously evolves along tests. To do so, results of [A] are used:

$$\varepsilon_3 = \varepsilon_3^{chem} + \varepsilon_3^{mech} \quad (1)$$

$$\varepsilon_3^{chem}(t) = \int_0^t CCS_3(t')dt' \quad (2)$$

the coefficient of chemical shrinkage being equal to -3.83% before the gel point ( $\alpha=52\%$ ) and to 2.07% after.



**Figure 2:** curing cycle and stress amplitude evolution (a) – creep-like compression tests (b).

## 3. RESULTS AND DISCUSSION

Typical results at different degrees of cure are presented in Figure 3. Strain and stress levels strongly evolve during curing, results were presented in terms of a normalized creep strain  $\varepsilon_3^*$  as:

$$\varepsilon_3^* = \frac{\varepsilon_3^{mech}}{\sigma_A} \quad (3)$$

$\sigma_A$  denoting the stress amplitude as defined in Figure 2(b). The composite clearly exhibits a viscoelastic behavior, with an initial elastic increase followed by a creep stage under constant stress, then by a more or less limited elastic return. It is to notice that the elastic return is always incomplete so that the material shows a viscoelastic liquid type of behavior.

In a second step, this viscoelastic behavior was further confirmed by the use of a 4 parameters Burgers model described in Figure 4(a) that enabled to reproduce the major trends observed experimentally. As shown in Figure 4(b), experimental curves can be pretty well fitted by such a model by a proper adjustment of the 4 parameters  $E_0, E_1, \eta_0, \eta_1$ . Among them,  $E_0$  controls the initial stiffness,  $\eta_0$  the creep viscosity, and the pair  $(E_1, \eta_1)$  control the viscoelastic response time.

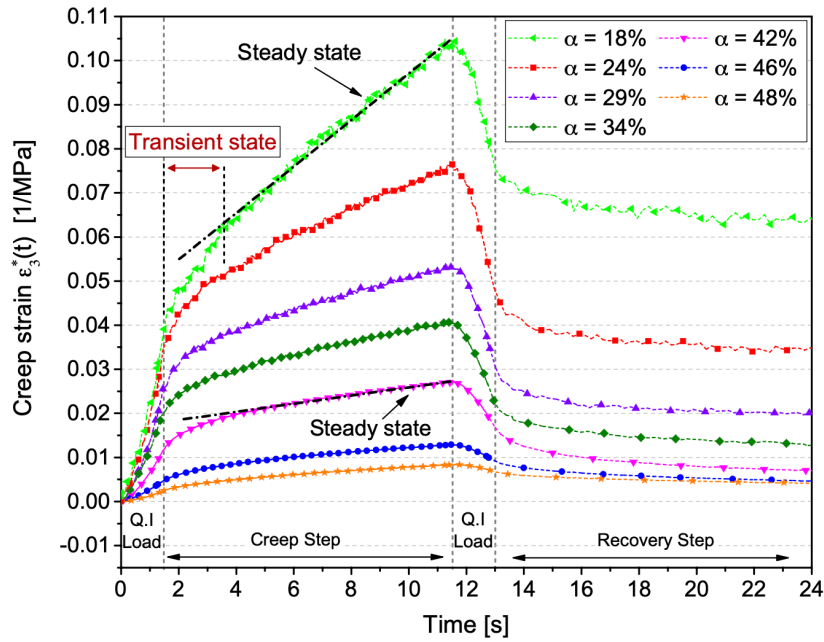


Figure 3: viscoelastic response obtained at different degrees of cure  $\alpha$ .

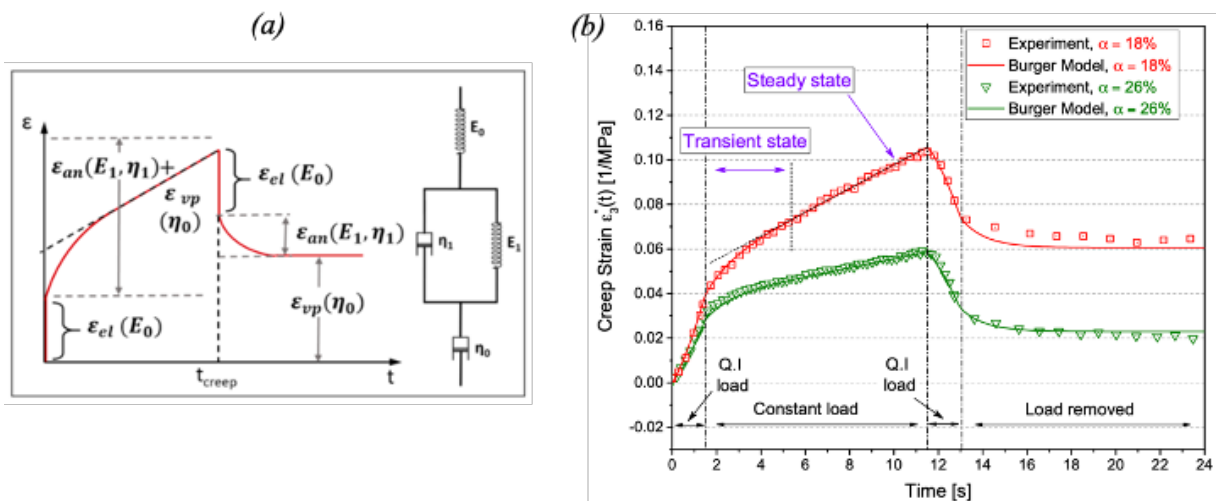
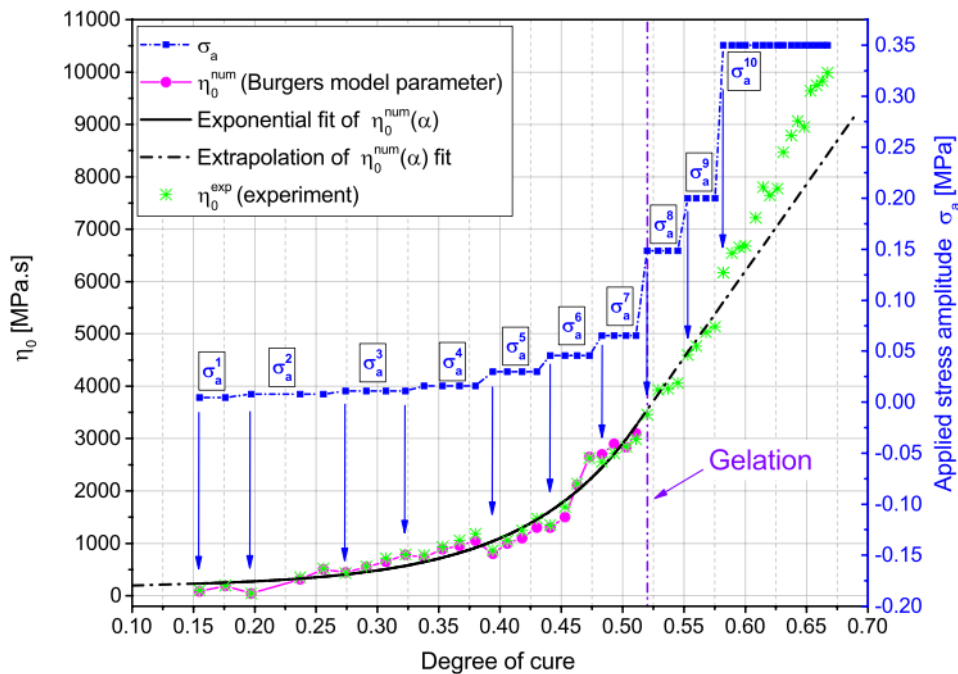


Figure 4: Burgers analogous model used for fitting (a) and example of fitting obtained on two different degrees of cure (b).

In a last step, a global fitting of Burgers model over the whole values of the degree of cure was performed. As illustrated in Figure 5 in the case of parameter  $\eta_0$ , an exponential evolution can be proposed and matches quite well the observed trend up to 55% of curing. Due to a problem of compliance of the device combined to the maximum load capacity of the testing machine, the estimation after this point is less reliable so that a simple linear fit was proposed, with a maximum weight on the first point after gelation. Doing so, one can obtain the rather good agreement observed on Figure 5. Proceeding in the same way for each rheological constant, one obtain the rheological functions  $E_0(\alpha)$ ,  $E_1(\alpha)$ ,  $\eta_0(\alpha)$ ,  $\eta_1(\alpha)$ , and can finally propose a fully cure-dependent viscoelastic Burger's model as:

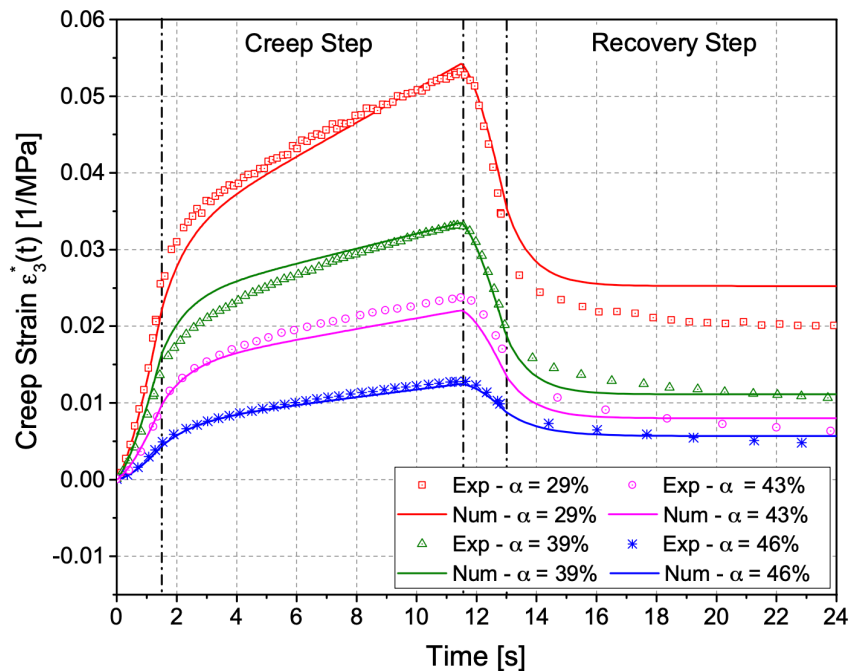
$$\frac{d\varepsilon}{dt} = \frac{1}{E_0(\alpha)} \frac{d\sigma}{dt} + \frac{\sigma(t) - E_1(\alpha)\varepsilon(t)}{\eta_1(\alpha)} + \frac{\sigma(t)}{\eta_0(\alpha)} \quad (3)$$

This model can easily be combined to the cure kinetics model of the epoxy resin and creep-recovery tests at each degree of cure and compared to experimental results presented above.



**Figure 5:** Global fitting of the  $\eta_0$  parameter all along the curing cycle, measurements are reliable up to 55% of curing.

As depicted in figure 6, though less precise than individual fittings at a given  $\alpha$ , the global model gives very satisfactory predictions over the curing cycle. Stress level and characteristic relaxation times are well predicted up to the gelation, located around 52% of curing.



**Figure 6:** Comparison at different degrees of cure between the experimentally determined creep-recovery behavior with those calculated according to the global Burgers model.

### 3. Conclusions

This contribution presents a novel experimental approach enabling a fine characterization of composites rheological properties along all the curing cycle, with a particular focus on the before gelation properties. Though material elasticity and viscosity are shown to evolve exponentially with the degree of cure, the viscoelastic behavior of liquid type is shown to be conserved up to 60% of degree of cure. Surprisingly, no yield stress could be observed on those tests although based on the use of stress ramps followed by creep stages. A complete viscoelastic model was identified and validated on the presented sequence of tests, as well as on other ones not presented here.

Further works should complete this complex analysis for other composites formulations, and check the continuity of the viscoelastic behavior after gelation with more conventional approaches as dynamic mechanical analysis (DMA) in compression mode, for instance.

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