EXPERIMENTAL CHARACTERIZATION OF THE VISCOELASTIC BEHAVIOR OF A CURING EPOXY MATRIX COMPOSITE FROM PRE-GELATION TO FULL CURE. APPLICATION TO SIMULATE RESIDUAL DEFORMATION

Alain Vinet[1], Sylvain Chatel[1], Jean-Marc Dupillier[2], Patrick Pérès[2]

[1] Airbus CRT 18 rue Marius Terce 31025 Toulouse,

[2] ArianeGroup, BP20011, 33165 Saint-Médard-en-Jalles

Abstract

Within a cure kinetics for a commercial epoxy well established, we proposed in this work to establish Time-temperature and Time-conversion superposition principles from pre-gelation to full cure material to predict residual deformation of the structure. To use viscoelastic-curing model on the material behaviour is not new. To have a continuum model with possibly dependence of Maxwell coefficient model with degree of curing is more complex to identify. Characterization has been done from both classical dynamic mechanical analysis and compressive creep test specimens loaded at 1 Mpa, closed to the manufacturing process.

For the last tests, creep deformations are recorded by image correlation system with an accuracy of microns. We compared these two methodologies to validate activation energies and final master curve of modulus. Tests have been done from temperatures of 40°C to 100°C, degree of cure of 0.6 to 1.0 and frequencies of 0.01Hz to 10Hz. Non classical identification of chemical and CTE properties have been performed. Comparison of experimental results with full viscoelastic model prediction will be discussed.

1 – **INTRODUCTION**

Understanding the cure of thermosetting materials is important to their application in the aerospace. The isothermal time-temperature-transformation (TTT) cure diagram of Gillham has provided and intellectual framework for understanding the behaviour of these systems during cure, particularly the effects of gelation and vitrification on the cure kinetics and properties. Here we propose two methodologies to identify strain behaviour during curing cycle process:

1- by creep test at stress level equivalent to the thermal expansion of the mandrel to be closed to the process even if fibbers are not under tension
2- by using classical Dynamic mechanical analysis in torsion to check that Arrhenius energy with G' - G'' interpretation

Even if many studies have been performed to model winding process at ArianeGroup, difficulties are still encountered to well predict the residual stresses without taking into account the influence of winding tension. The compaction of the composite is governed by the tension of the tow and mainly by the thermal expansion of the mandrel. In this works, we try to identify continuum model under and above gelification corresponding to winding – resin “maturation and polymerisation manufacturing steps.

2 – **TESTS AND SPRING-IN RESULTS ON $[90]_{20}$ lay up**

2.1- Creep test on curing specimens

First of all, creep test have down on specimens from different degree of conversion like 0.65, 0.75, 0.85 to 0.95 tested at four temperatures 40°C, 60°C, 80°C and 100°C corresponding to step of the process. Dedicated test facility have been developed at CRT to make these tests in situ by measuring displacement by images correlations as presented in the two next figures :

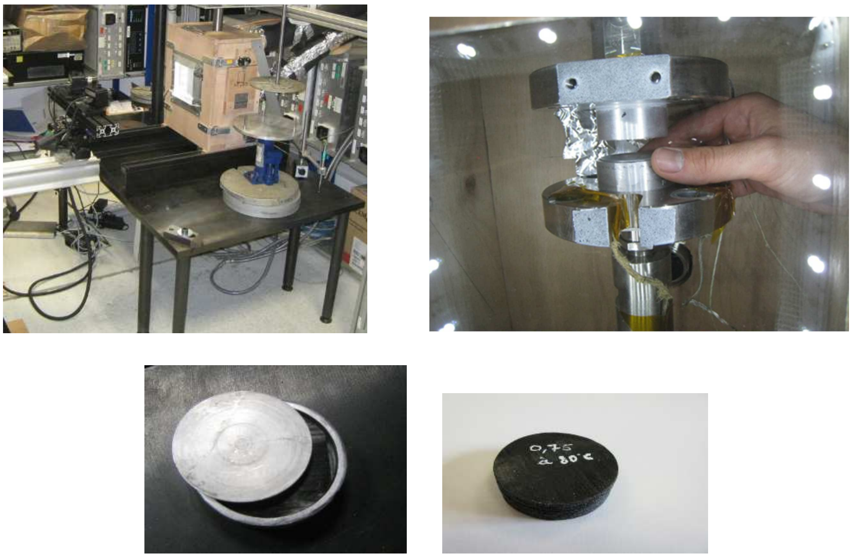

Figure 1*: Dedicated test facility with its specimen developed by CRT*

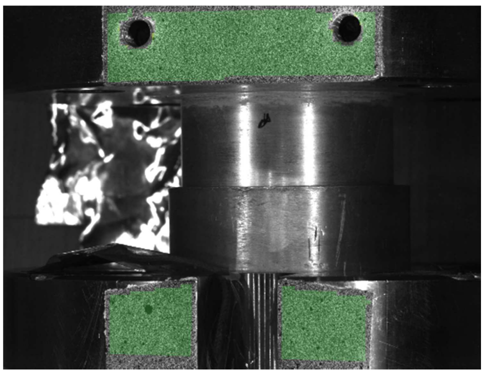

Figure 2*: Painted stress parts for image correlation*

Tests results à 100°C at different conversion degree are presented on the next figure and show a break behaviour between α=0.85 and α=0.79 that it supposes that gel point is between these two values.

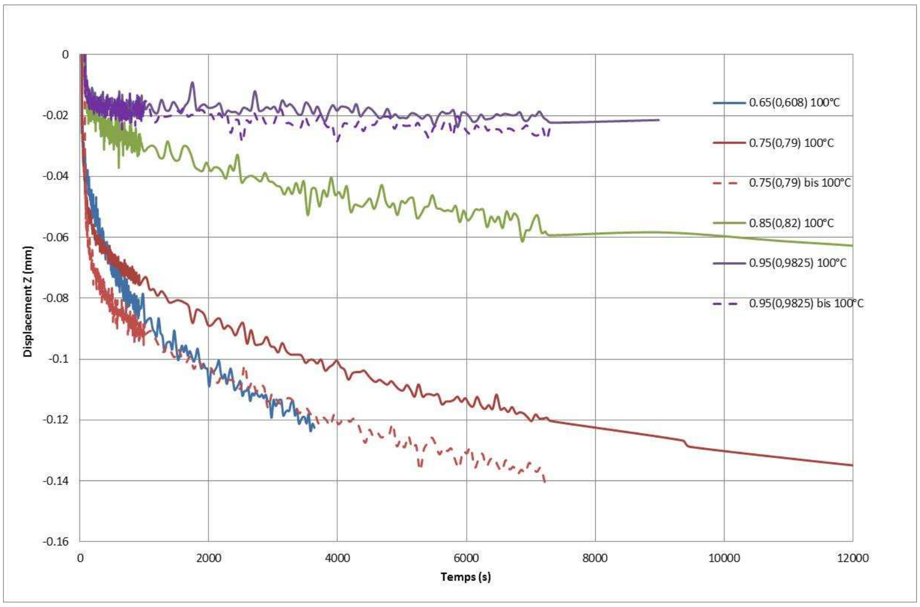

***Figure 3**: Compression creep displacement results at 100°C on specimen at degree of conversion from 0.65 to 0.98*

During these tests, elastic modulus are not correctly identified and tensile tests have been performed to make the part between elastic and viscoelastic components. For these tests, it was non-possible to apply principle of time-temperature and time cross-link density superposition for all temperatures and conversion degree. Therefore, when using writing strain with a function of stress, we identified Prony series for viscoelastic model depending on temperature and conversion degree following the manufacturing process.

$$\varepsilon_{ve}(t) = D_0\sigma + \int_0^t \Delta D(\xi(t) - \xi(\tau)) \frac{d\sigma(\tau)}{d\tau} d\tau$$

With $\xi = \int_0^t \frac{1}{a_T} dt$

$$D(\xi,\alpha) = D_0(\alpha,T) + \sum_{i=1}^{n} D_m(\alpha)(1-\exp(-\xi/\tau_m(\alpha))$$

Parameters of prony series are presented in table 1.

α	α reel	temperature	D1	D2	D3	D4	tau1	tau2	tau3	tau4
0.65	0.61	40.00	2.05E-02	0.01210162	0.00290514	0.02112997	1.66666667	1.67E+01	1.67E+02	1666.66667
0.65	0.61	60.00	1.94E-02	0.02290423	0.00142547	0.005304	1.99526232	39.810717	794.328235	15848.9319
0.65	0.68	80.00	1.87E-02	1.22E-02	2.58E-03	1.05E-02	2.51188643	63.0957345	1584.89319	39810.717
0.75	0.79	100	3.23E-02	1.88E-03	1.44E-03	8.10E-03	1.58489319	2.51E+01	3.98E+02	6.31E+03
0.85	0.82	100	2.49E-02	4.43E-05	7.65E-04	5.04E-03	1.58489319	2.51E+01	3.98E+02	6.31E+03
0.95	0.9825	100	6.81E-03	9.91E-05	1.69E-03	1.00E-08	5.01187234	2.51E+02	1.26E+04	1.00E+05

***Table 1**: Prony series parameters depending on α and T*

Tau_i and Di are written as a continuum function of temperature and conversion degree. At fully cured state, using WLF equation for temperature acceleration, C value is equal to 312 K-1.

Elastic modulus have been identified by both tensile and DMA tests.

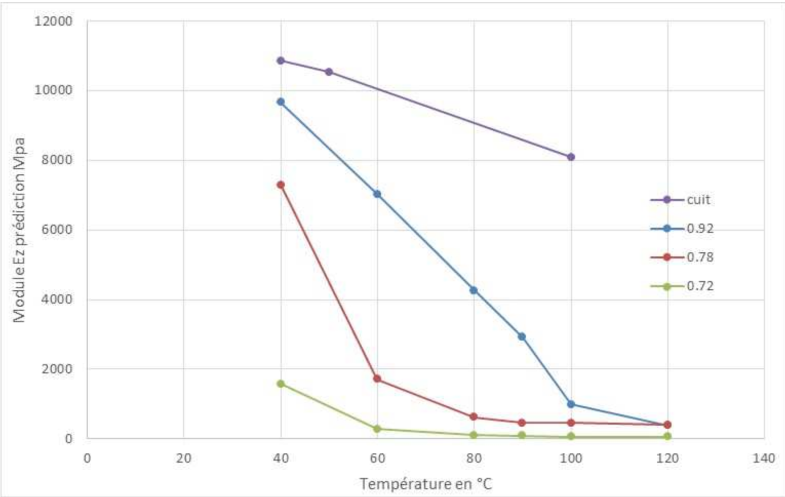

Figure 4*: Evolution of compression modulus with* α *and T*

With viscoelastic model depending on α and T with thermal and chemical deformation characterised by CRT, we make an estimation of the spring-in of 5 mm with aluminium mandrel. This numerical result doesn't match to experimental measurements and doesn't take into account of the tension of the winded fibres.

Figure 5*: Evolution of residual strain gradient on composite after curing on* $[90]_{20}$ *lay up*

It seems that creep strain characterised with compressive transverse loading is not sufficient to reach the 19 mm spring-in evaluated by test measurement. Identications tests difficulties are the optimization of the crucible with the specimen to avoid either bulk behaviour or sling behaviour. Many tests have be done in the same configuration and show the same creep strain evolution but the elastic response was somewhat different. Recall that elastic modulus have be tested only at fully cured state and not at lower level conversion degree. Further tests have to be handled in order to complete this approach.

2.2 - Dynamic mechanical analysis in torsion

Figure 6: *Dynamic mechanical analysis in torsion at CRT*

The modulus of thermosetting material with a given conversion is a function of time or frequency and temperature. The storage and loss moduli can be approximated by a sum of Maxwell elements.

$$E(t) = E_r + \left[E_g - E_r\right]\sum_{i=1}^{n} g_i e^{\frac{-t}{\tau_i}} \quad (1)$$

with

$$E^{'}(\omega) = E_r + \left[E_g - E_r\right]\sum_{i=1}^{n} g_i \frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2} \quad (2)$$

and

$$E^{''}(\omega) = E_r + \left[E_g - E_r\right]\sum_{i=1}^{n} g_i \frac{\omega\tau}{1+\omega^2\tau_i^2} \quad (3)$$

With Eg is the glassy value of the modulus that is not a strong function of temperature. Er is the rubbery modulus that is a function of both temperature and conversion, t is a time and w is radian frequency. τi is the i_{th} relaxation time and g_i is the weighting factor for the i_{th} relaxation time such that the sum is equal to one. According to McKenna and all above Tg, the effects of temperature and conversion on the relaxation time are accounted for by applying the principles of time-temperature and time-cross link density superposition. We use both a temperature and conversion shift factor to account for the temperature and for the cross-link density dependence of relaxation time: $\tau_i(T_g) = a_x\tau_i(T_g x_{ref})$. The effects of temperature can be modelled both by Arrhenius law and by WLF according to the temperature of the material with its Tg. Mc Kenna combines these equations such as:

$$\log a_{Tx} = \log \frac{\tau_i(T, Tg(x))}{\tau_i(T_{ref}, Tg(x_{ref}))} = \left(\frac{C_T}{T - T_\infty} - \frac{C_T}{T_{ref} - T_\infty} \right) - \left(\frac{C_x}{T_g(x) - T_\infty} - \frac{C_x}{T_g(x_{ref)} - T_\infty} \right)$$

with $T_\infty = Tg - C_2$ and DeBenedetto equation to predict Tg

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda) x} \quad (5)$$

We performed DMA torsion tests within 0.5 – 65 Hz from 40°C to 120°C at three degrees of conversion checked by DSC tests specified on table 2

Tg	83°C	66°C	36°C	26°C
α	0.978	0.92	0.782	0.72

Table 2: *Synthesis of a and Tg of tested specimen in DMA*

Identification methodology suggested by Mc kenna is to establish time temperature principle at fully cured of the material. Master curve is identified for reference temperature 40°C with limited temperature test. We notice a break behaviour when test temperature is closed to 90°C Tg value.

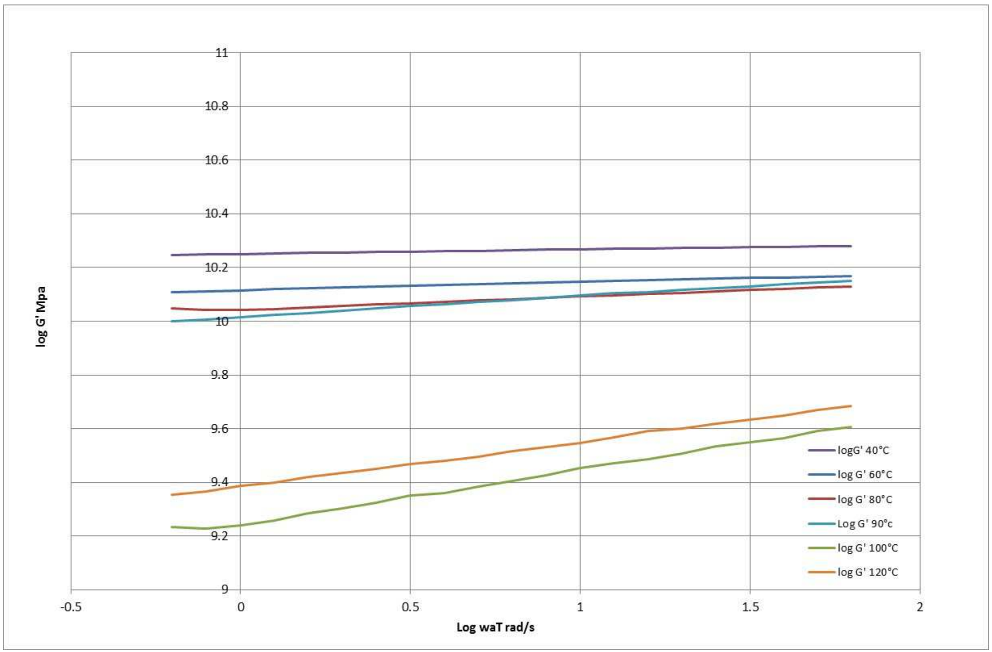

Figure 7*: Logarithmic representation of the storage modulus vs frequency for fully cured material*

Identification of master curve G(t) at fully cured is based on identification of G'(w) master curve obtained by using a least-squares regression to find the weighting factors for the relaxation times. Based on a &2 analysis, the average relaxation difference between the data and the fits is less than 5 %.

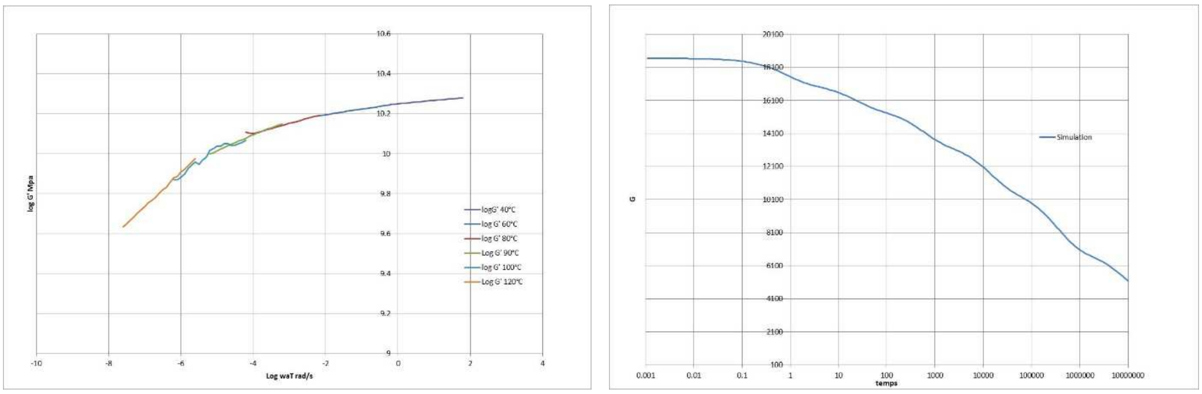

***Figure 8**: Logarithmic representation of log G'(w) and G(t) with reference temperature 40°C at fulled cured*

Checking that this principle is available for lower conversion degree material under gel point, we obtained four master curve with only the effects of temperature and unique with both effects of T and α presented on the next figure:

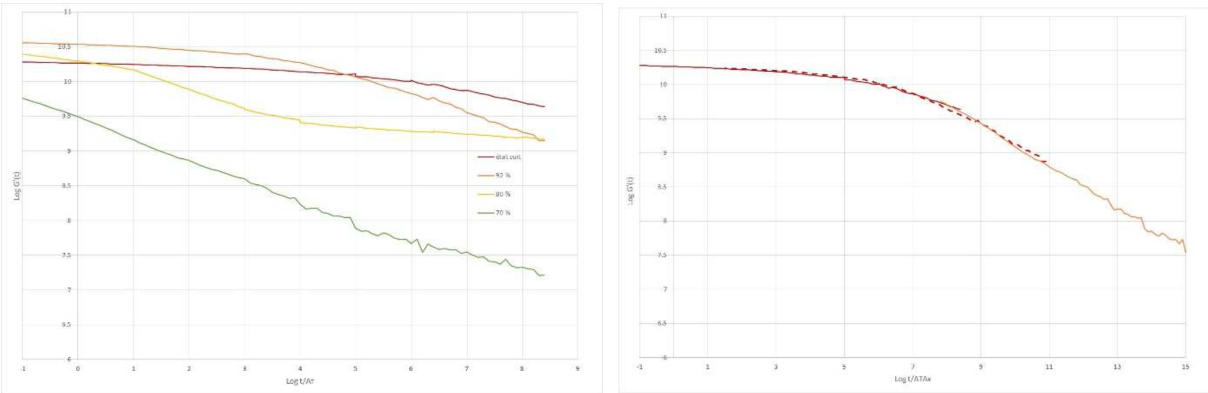

***Figure 9**: Logarithmic representation of log G'(t/a_{Tx}) at reference temperature 40°C at 92%, 80 %, 70% and fulled cured and final master curve*

We succeed in making superposition cross-link by shift factor at level conversion supposed under gel point. With this new identification, we make a numerical estimation of the spring-in of 14 mm with aluminium mandrel better closed to the test results. Sensitivity of resin properties as resin shrinkage and resin CTE have been well characterized by Airbus CRT. The major contribution in spring effect is brought by mandrel thermal expansion and in second manner by resin cure shrinkage. Higher mandrel CTE cause higher residual stresses. Thermal gradient (the outer layer being hotter than layer in contact with mandrel) has low influence in spring-in.

If we simulate thermal, shrinkage strain and curing strain of the outer composite ply we obtain these following figures:

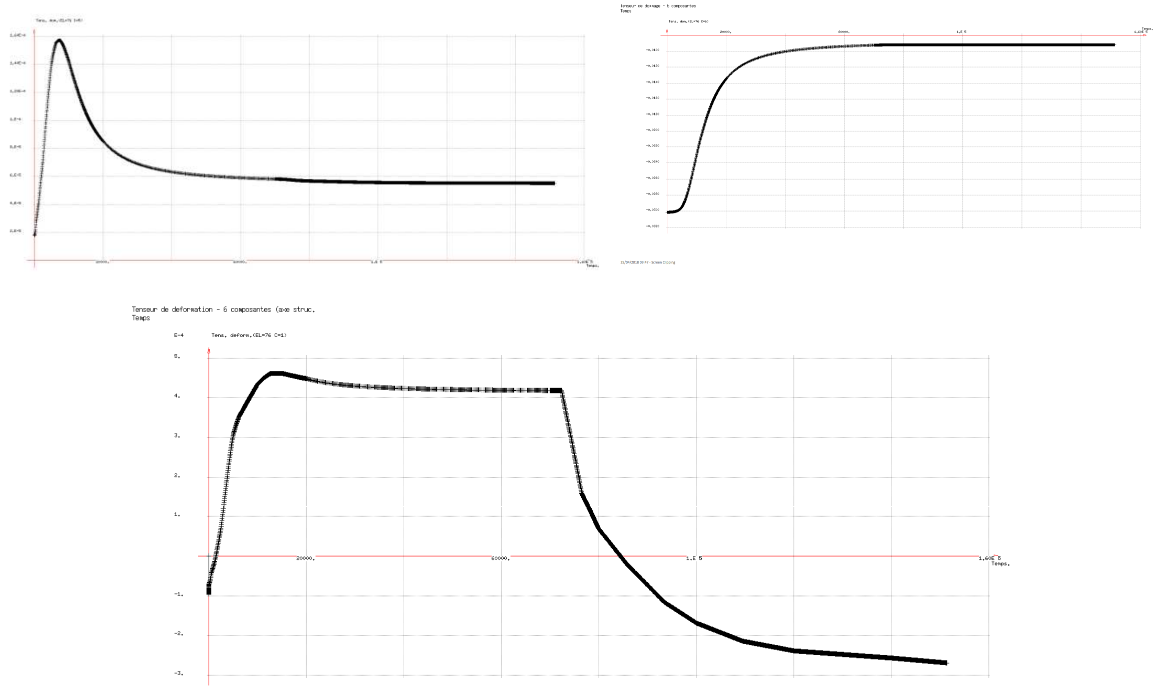

***Figure 10**: Evolution of outer ply x strain, CTE2 and CH2 thermal shrinkage transverse component during manufactured cycle process.*

5 – Conclusions

Two methodologies have been applied to identify viscoelastic behavior during curing of thermosetting material. One has been done by creep compressive test on (0/90/0/90)ns lay up and the other one on Dynamic mechanical torsion. It is established that creep in shearing loading is higher than creep for transverse loading. But, the conclusions are that parameters identified by DMA make a better prediction of the (90)20 lay up spring-in. WLF C coefficient are really too different between these two methodologies. Then, time –temperature link-cross could be applied on storage modulus until 70 % of degree conversion which supposes that this value is above gel point.

6 – References:

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