Experimental Characterization of the Viscoelastic Behaviour of a Curing Epoxy Matrix Composite from Pre-gelation to Full Cure. Application to Simulate Residual Deformation

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Content

Context and objective

Ariane Group Structure:

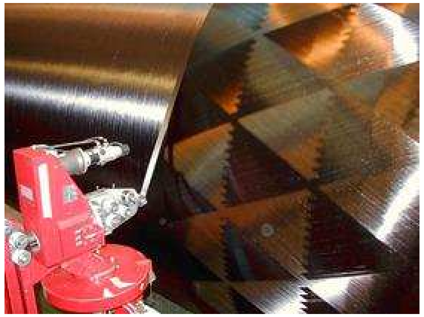
- 90° rings, thermoset 120°C
- Winding technology

Manufacturing steps:

Preparation roving yarn

→

Winding



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Resin "maturation"

1 week

→

Polymerization

Tg	*-10°C*	*5°C*	*25°C*		*100°C*
α	*Lower than 1%*	*20%*	*70%*	*Gel point ≈ 80°C, 85%*	*100%*

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Context and objective

Conclusion of preliminary studies (extract of Ariane Group comments): at the beginning for CRT project

- ❑Prediction of the tension relaxation during winding: **Fair**
- ❑Prediction of the evolution of the fiber volume fraction: **Preliminary results to be confirmed**
- ❑Prediction of the pressure evolution on the mandrel: **Fair for winding phase – to be improved for curing**
- ❑Prediction of the residual strain/deformation after curing: **Poor with the current Chile model proposed**

*Under estimation of the spring-in

*The effect of the winding tension in spring in is not well predicted.

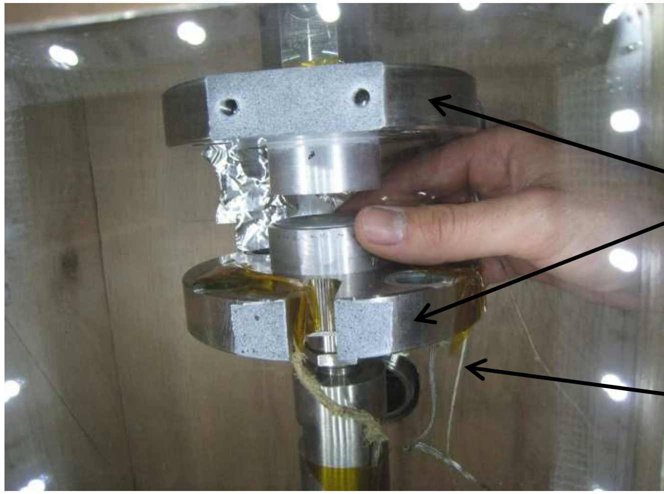
Objective of tasks:

Development of new experimental approaches for identification of viscoelastic behaviour during manufacturing steps (before and after gel point, viscoelastic history in function of resin state) with DMA and Creep compression tests closed to the process.

“Creep compression” test

Development of new test bench “creep compression” for identification of viscoelastic behavior:

- To be closed to the manufacturing process (1Mpa) corresponding to thermal deformation of mandrel on composites
- Adapted thickness specimen with gradient thermal behaviour



“Creep compression” test

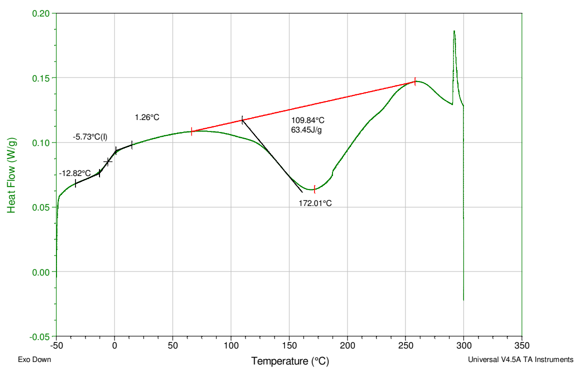
Testing procedure:

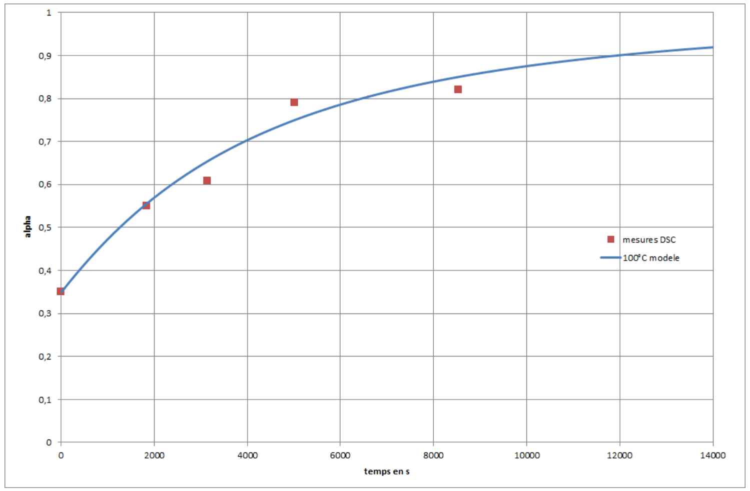
1) Measurement of initial thickness (α=0.35) *Ariane Group preparation*

Lay-up (0/90/0/90/0)8.
Targeted thickness 10mm.

2) Pre-curing to target α witched (in oven or testing machine)

3) Verification of degree of cure with DSC and Di Benedetto model





$$Tg_{(\alpha)} = Tg_0 + (Tg_0 * a * \alpha / (1 - (1 - b) * \alpha))$$

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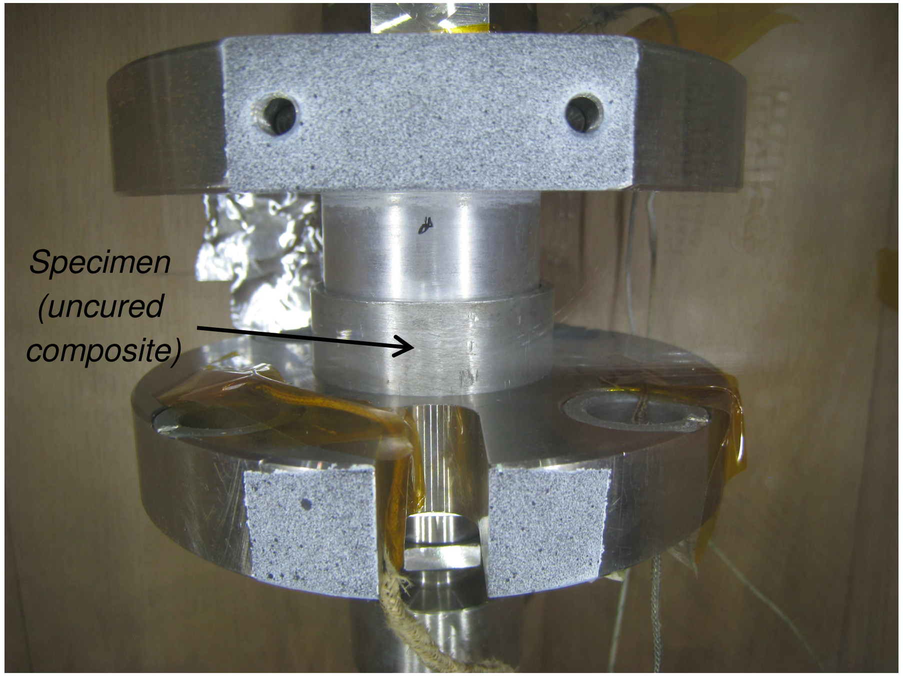
“Creep compression” test

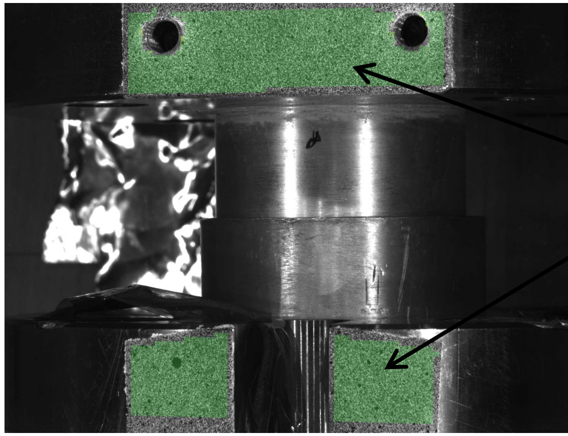
Testing procedure :

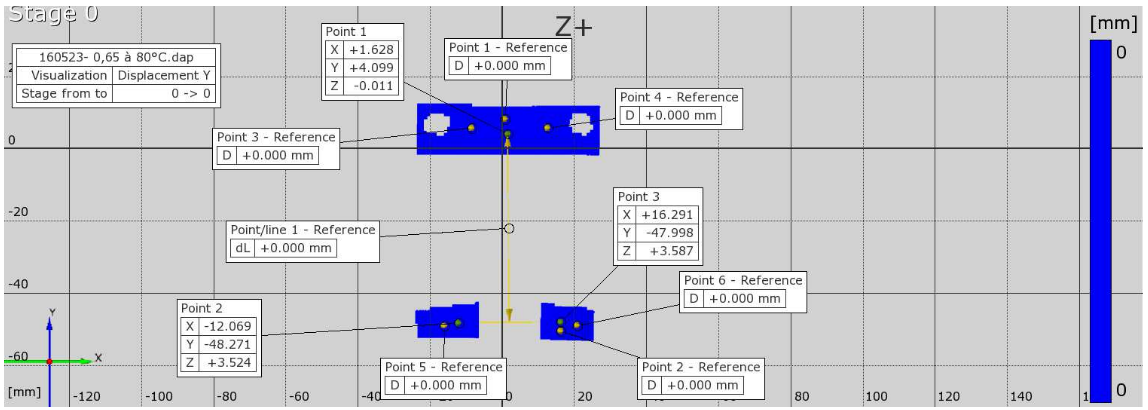
4) Application of compression and measurement of displacements

Images correlation methodology:

One image per second at the beginning and lower during creep test (across the oven)





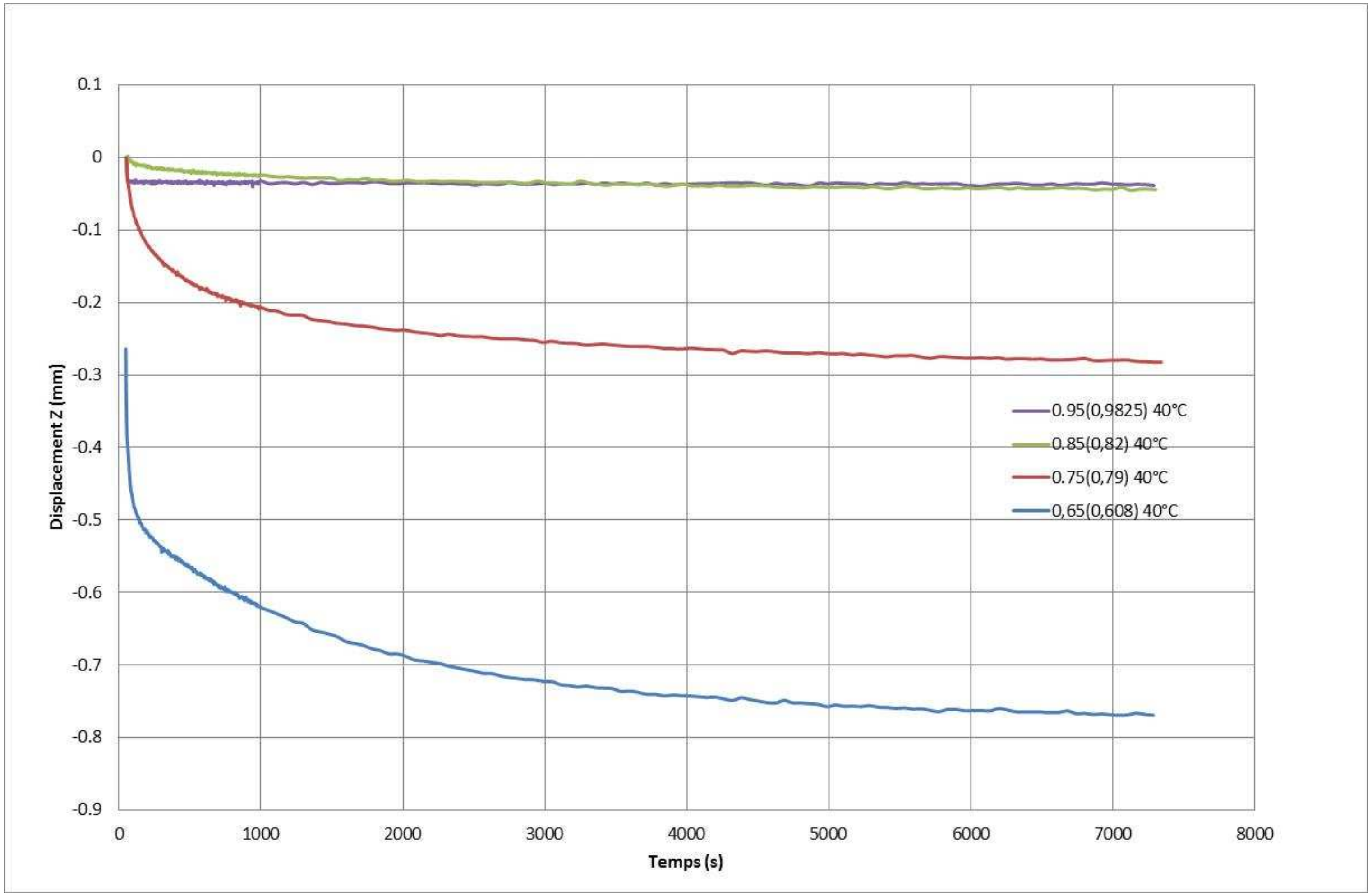


"Creep compression" test

Results:

Creep compression performed at 1 MPa for 100°C, 80°C, 60°C and 40°C with α from 0.6 to 0.98

40°C
Without elastic component
Gel point 0.9



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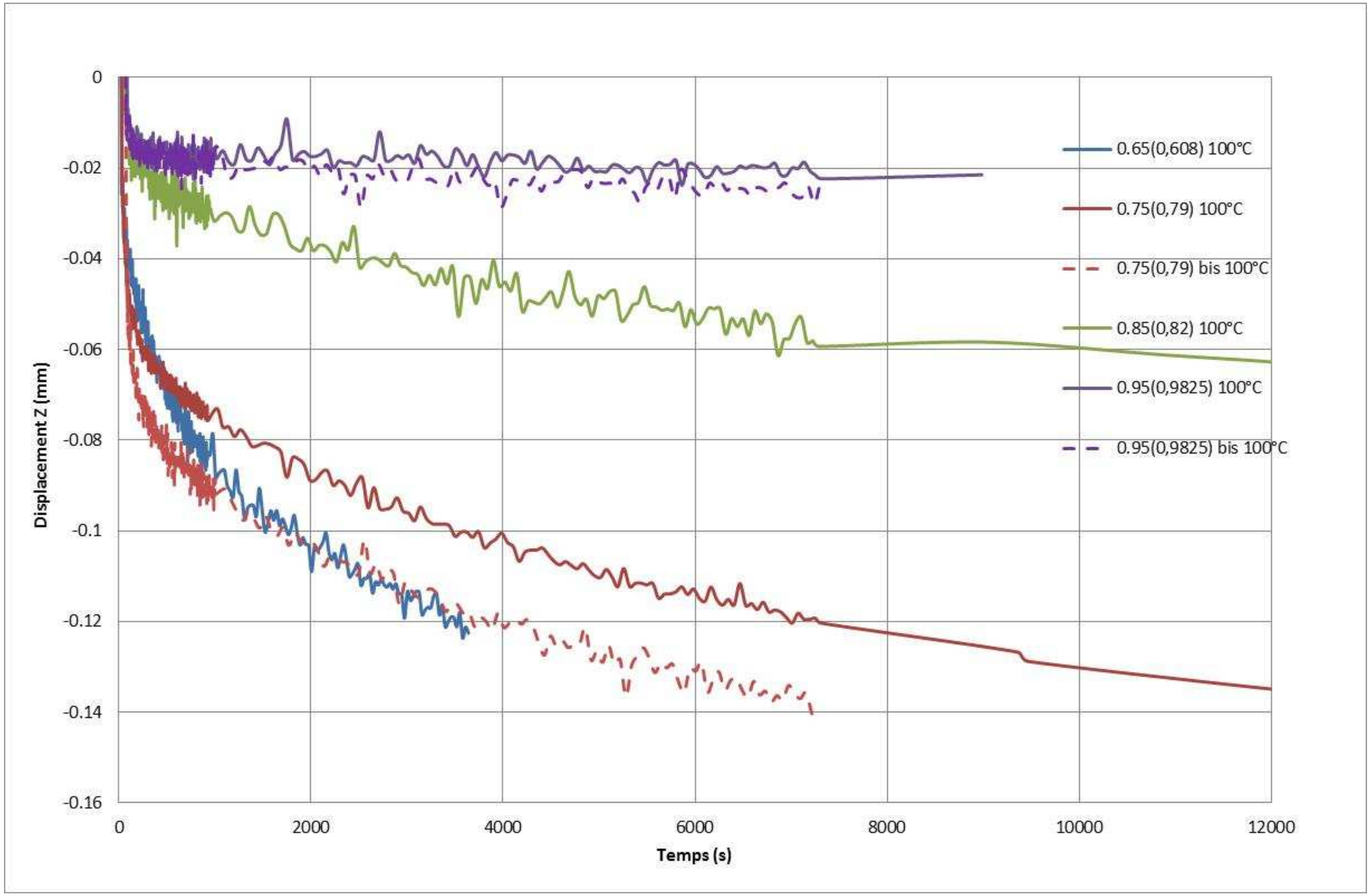

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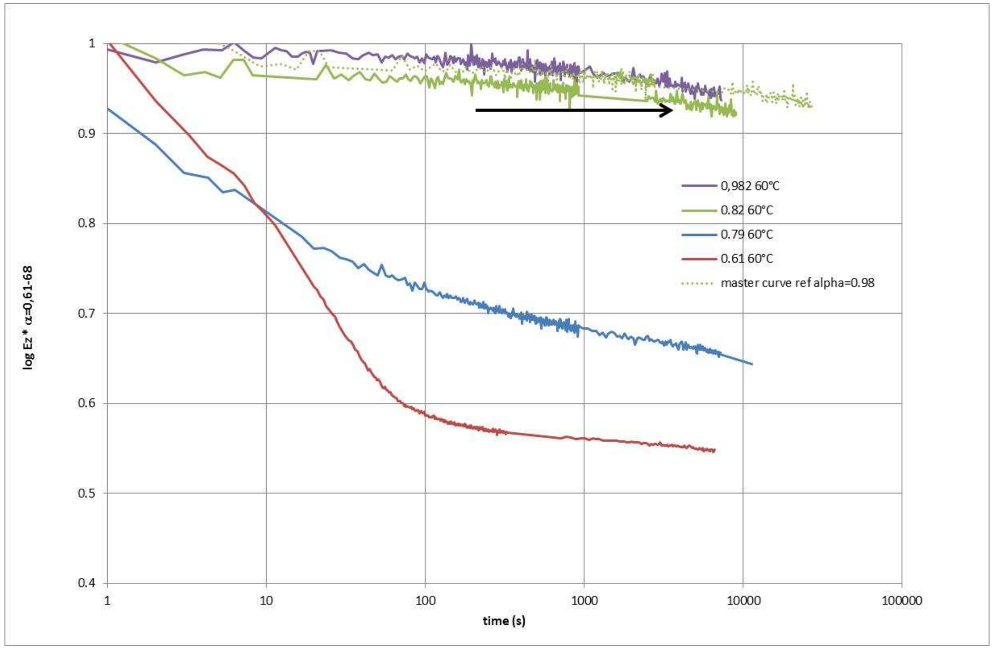
Viscoelastic behaviour identification with 'Creep compression" test

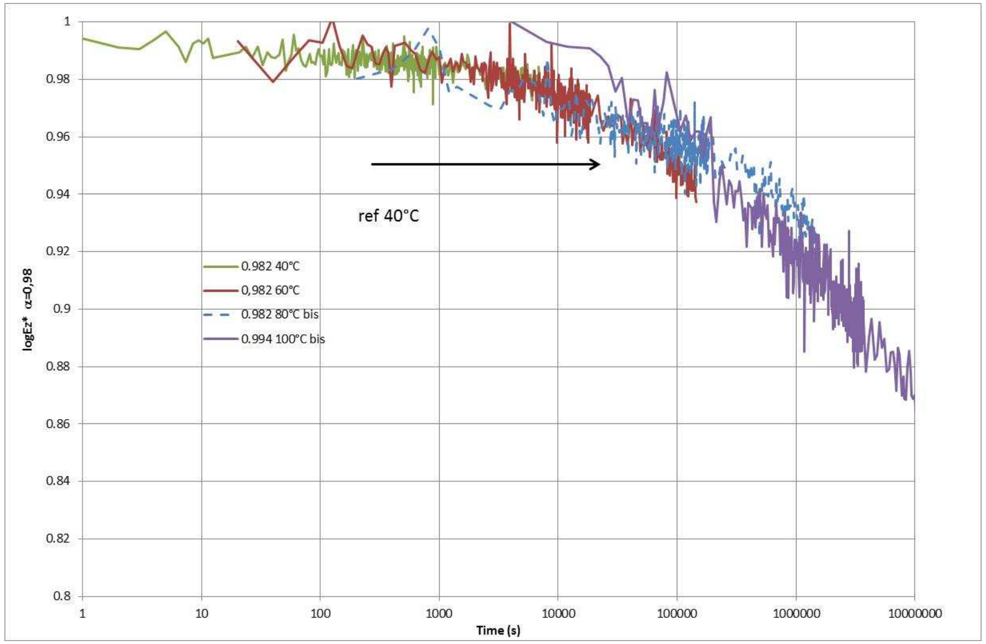
Viscoelastic modules evolution

- 2 superposition principle : time - temperature & time – degree conversion
  after gel point for epoxy resin (from Literature, Mc Kenna and al 1999) for α >0.82

- Not possible to construct master curve in order to expand the range of analysis



Creep tests at 60°C degree



Master curve at fully cured conversion degree

- No unique master curve has been identified within temperature from 100°C, 80°C, 60°C and 40°C with α from 0.6 to 0.98. Only master curve available for α from 0.82 to 1.

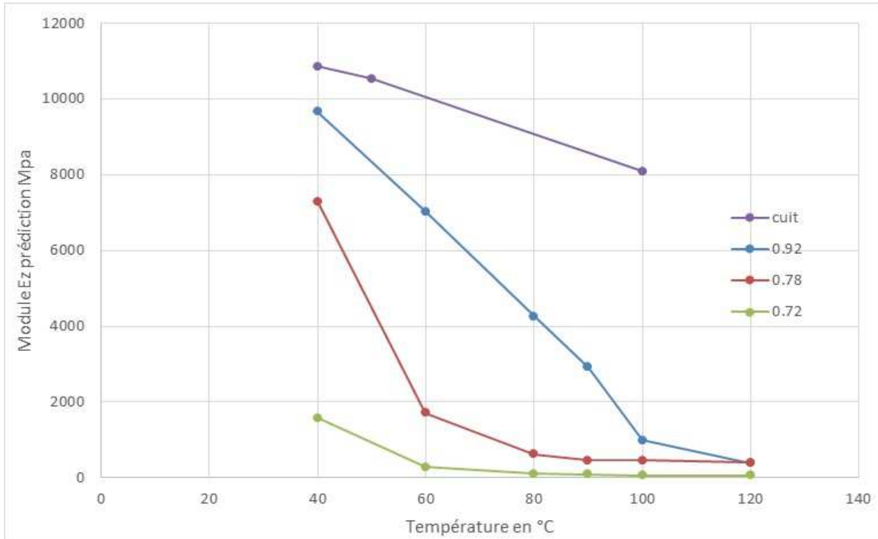
Viscoelastic behaviour identification with Creep - Creep recovery" test

Viscoelastic modules evolution

- Relaxation times seem depend on degree conversion using classical viscoelasticity equation with Prony series to describe compliance function

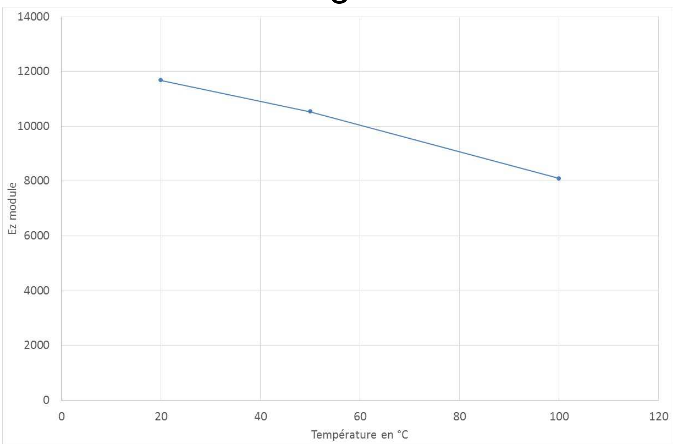
$$\varepsilon_{ve}(t) = D_0\sigma + \int_0^t \Delta D(\xi(t) - \xi(\tau)) \frac{d\sigma(\tau)}{d\tau} d\tau \qquad \xi = \int_0^t \frac{1}{a_T} dt \qquad D(\xi,\alpha) = D_0(\alpha,T) + \sum_{i=1}^{n} D_m(\alpha)(1-\exp(-\xi/\tau_m(\alpha))$$

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



Characterisation of elastic modulus both by tensile and DMA tests

- With this methodology, Prony series are depending on conversion degree and temperature which permit continuum model approach to predict viscoelastic behavior under and above .gel.



Compressive elastic test at Full cured state 20°C

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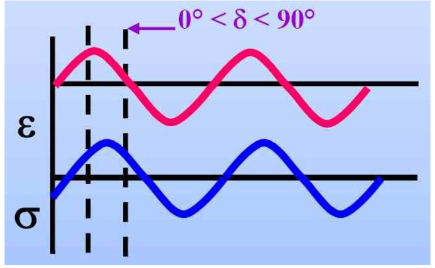
DMA Torsion Frequency test

Viscoelastic material using dynamic mechanical analysis

- *Time-temperature superposition principle*
- *Oscillation applied (sinusoidal)*



δ *: phase angle*

Dynamic mechanical analysis in torsion

$$\overset{*}{\gamma} = \frac{\theta.h}{L}$$ *with*

- * *: shear amplitude*
- θ *: shearing angle in torsion, imposed*
- *h,* $\mathcal{L}$ *: thickness and length of sample,*

Complex torsion moment : recorded

$$\overset{*}{\tau} = K.\frac{L}{b.h^3}.M^*$$ *with*

- $\overset{*}{\tau}$ *: complex shearing stress*
- *b, h : width, thickness of sample*
- *K : experimental constant based on form factor*

$G^* = G' + i.G''$ — *G*: complex dynamic module*

$$G' = \overset{*}{\tau}.\cos\delta$$

$$G'' = \overset{*}{\tau}.\sin\delta$$

G', G" : real and imaginary part of shearing module

$$\text{tg}\,\delta = \frac{G''}{G'}$$ *: loss factor*

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

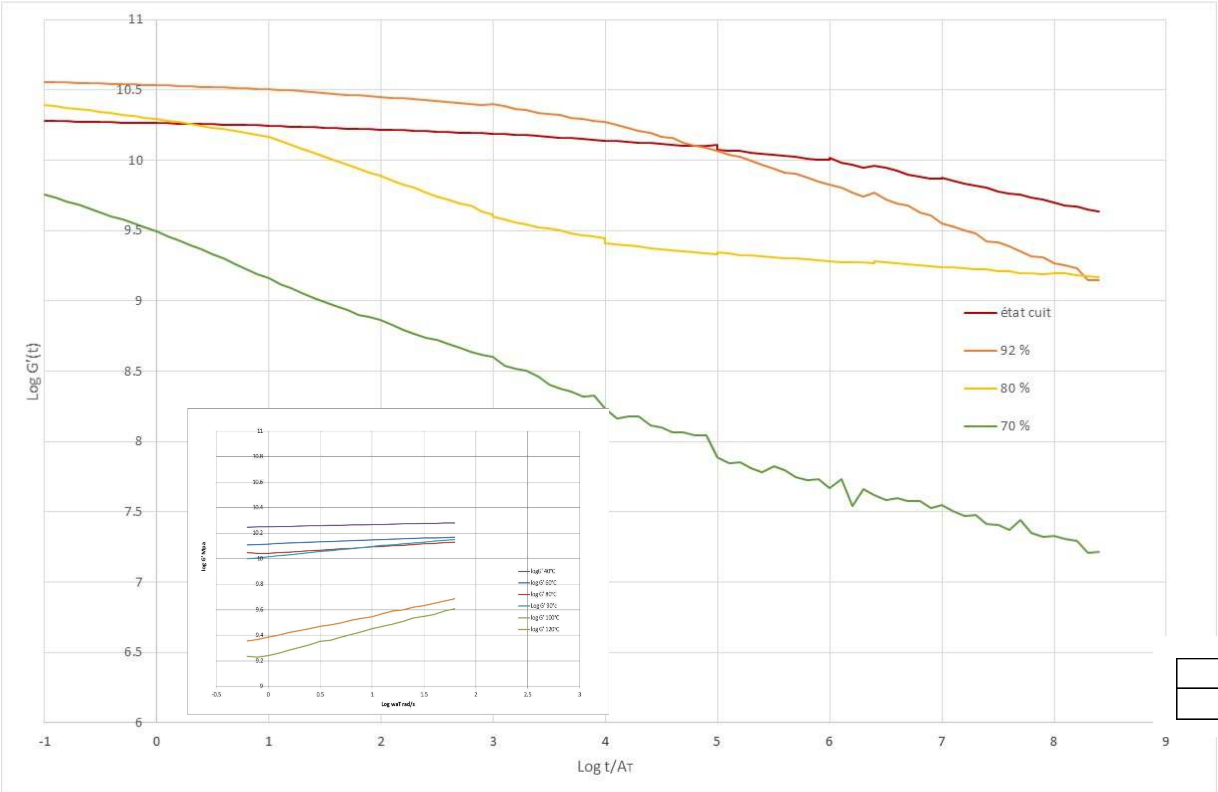
$$E'(\omega) = E_r + [E_g - E_r]\sum_{i=1}^{n} g_i \frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2}$$

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

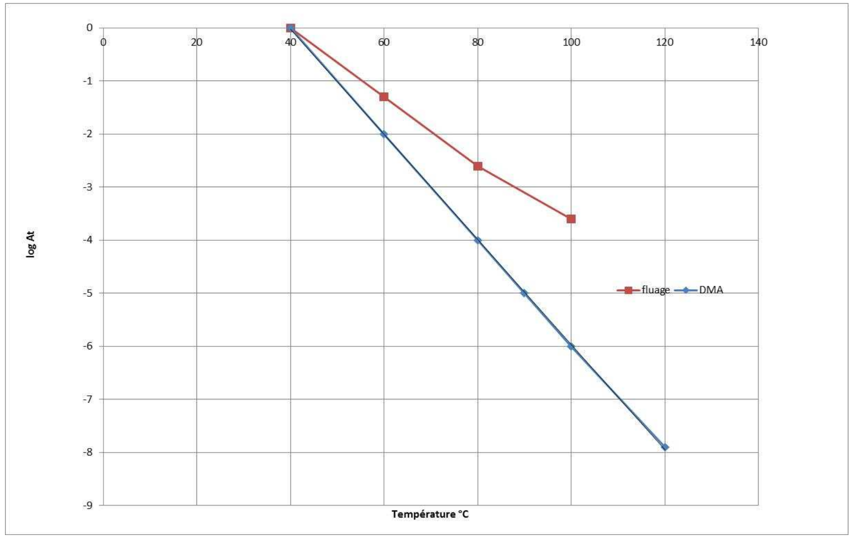
DMA Torsion Frequency test

Viscoelastic material using dynamic mechanical analysis

Tests have be down for temperature from 40°C, 60°C, 80°C, 90°C to 120°C on conversion degree composite material from 0.7 to 1. Master curve has been established at full cured to identify time – temperature principle superposition. DMA temperature tests are over Tg materials.



Log G'=f(t/aT) with conversion degree with application of TTSP on all logG' curve



Evolution of Log(aT) with DMA and Creep –Creep recovery tests at full cured

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

$$\psi = \int_0^t \frac{1}{a_T} dt \quad \text{with } \nabla\alpha \qquad \log a_T = \log \frac{\tau_i(T)}{\tau_i(T_{ref},)} = \frac{C_T}{T - T_\infty} - \frac{C_T}{T_{ref} - T_\infty}$$

Many results (1) indicate that when T-Tg>30°C TTSP application is complex because of effects of free volume. Arrhenius and WLF

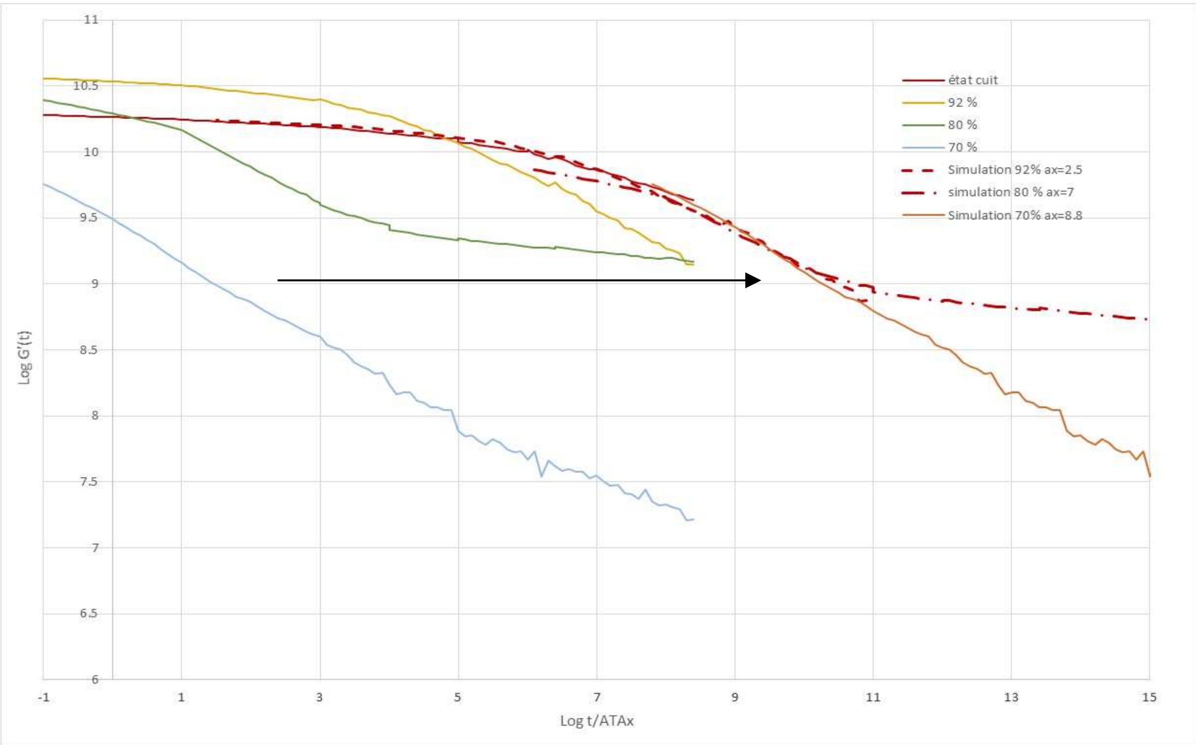
[1] Characterization of the viscoelastic properties of an epoxy molding compound during cure M. Sadeghinia Microelectronics Reliability 52 (2012) 1711–1718

DMA Torsion Frequency test

Viscoelastic material using dynamic mechanical analysis

Maxwell model have been used to convert G' test results with equivalent G(t) or E(t) value at full cured resin

$$E^{'}(\omega) = E_r + [E_g - E_r]\sum_{i=1}^{n} g_i \frac{\omega^2 \tau_i^2}{1+\omega^2 \tau_i^2} \Longrightarrow E(t) = E_r + [E_g - E_r]\sum_{i=1}^{n} g_i e^{\frac{-t}{\tau_i}}$$



Master curve Log G'=f(t/aTaα) TTSP + TαSP

According to McKenna approach TTαP is only acceptable for α> αgel but in our situation all the curve at lower α could be on one unique master curve contrary to creep-creep recovery tests analysis. So, we have :

$$D(\xi,\alpha) = D_0(\alpha,T) + \sum_{i=1}^{n} D_m(\alpha)(1-\exp(-\xi/\tau_m(\alpha)) \quad \text{n=8}$$

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

With De Benedetto Tg law

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1-(1-\lambda)x} \qquad T_\infty = Tg - C_2$$

Identified coefficients C2=330K, CT= 9479K and Cα=13023, Tref=273+40K, αref=1

[1] Modeling the evolution of the Dynamic Mechanical Properties of a Commercial Epoxy During Cure after Gelation. Journal of applied Polymer Science Vol 76, 495-508(2000) Simon, McKenna, & Sindt, 2000

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Chemical and Thermal evolution on cured – uncured material

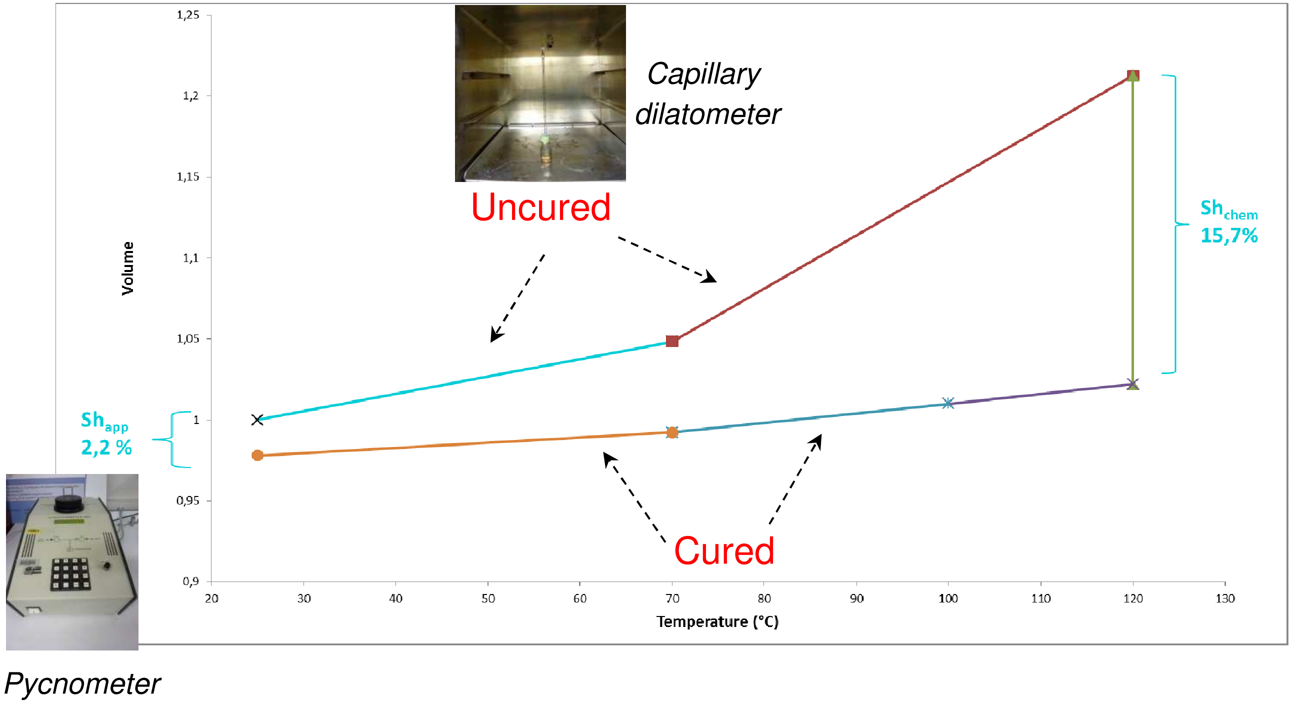
- Identification of chemical shrinkage

Density:

- Uncured state: 1,134 +/-1%
- Cured state (ArG values): 1,14 +/-0,02

Volumetric shrinkage (resin only)

- At polymerization temperature: 15,7%
- Cured state: 2,2%



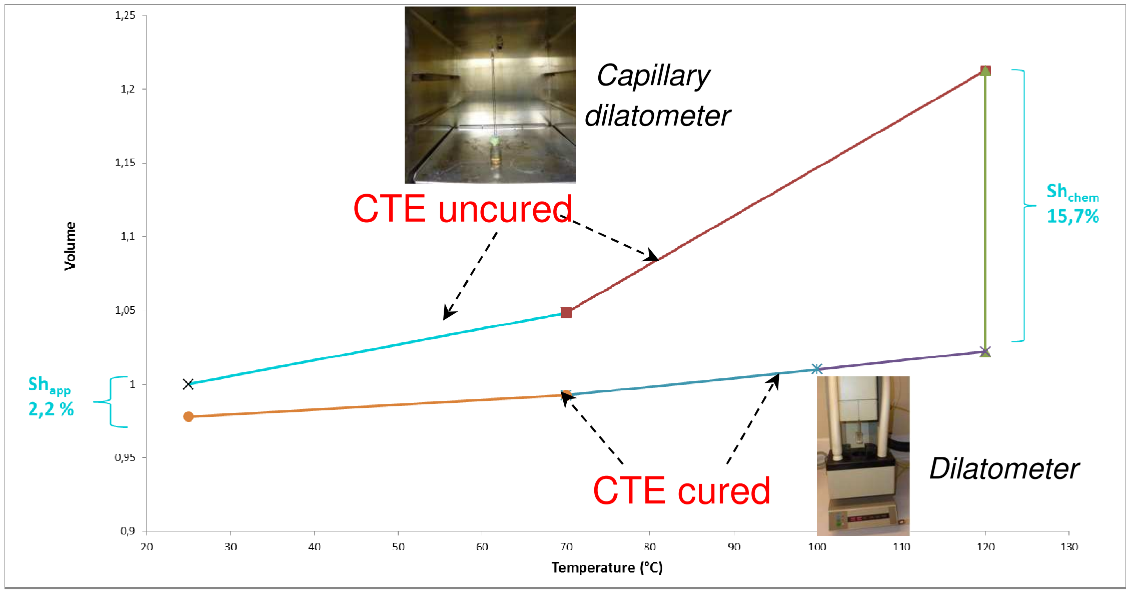
- Identification of thermal deformation

CTE un cured state:

- 350 um/m.°C +/-10% from T°amb to Tg
- 1000 um/m.°C +-10% from Tg to 120°C

CTE cured state :

- 200um/m.°C +/-10% from 120°C to 100°C
- 100um/m.°C +/-10% from Tg to T°amb



Synthesis on introduction Viscoelastic behavior on curing model

- Results of these two kinds of test are clearly different of the behaviour for curing deformation

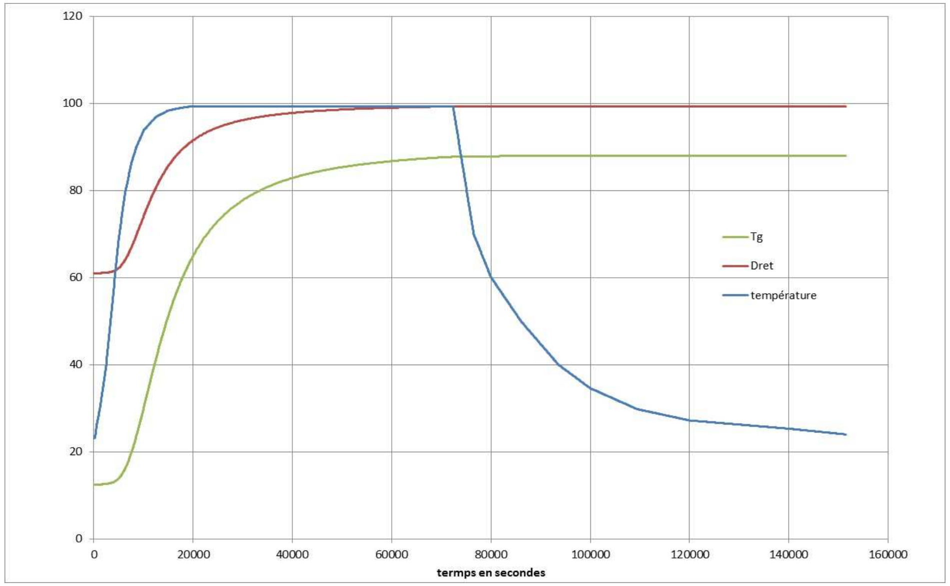
  - Creep-Creep recovery tests : behaviour under and above .gel is clear and different and no unique master curve could be established (only for α from 0.82 to 1). Continuum model is applied with effect of temperature and conversion degree on Prony series.

  - DMA Torsion frequency tests : continuum behavior is observed which supposes that α gel is under 70 % of conversion degree whereas its value is supposed between α 0.8 and 0.9. Master curve with Mckenna principle TTSP and TTαP could be applied with test temperature T-Tg superior to 80°C

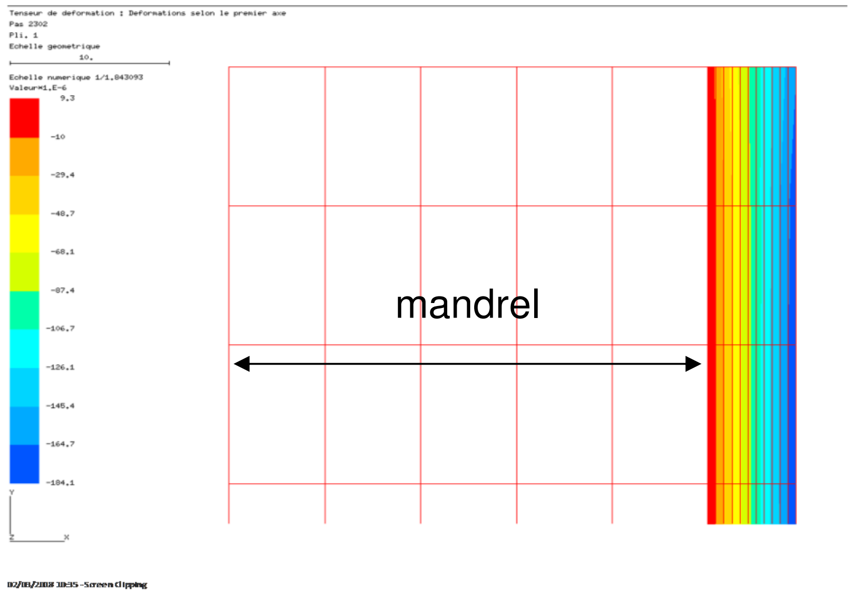
  - Activation Energy of TTSP have been identified different between these two tests at full cured state.

Simulation of Spring-in and Conclusions

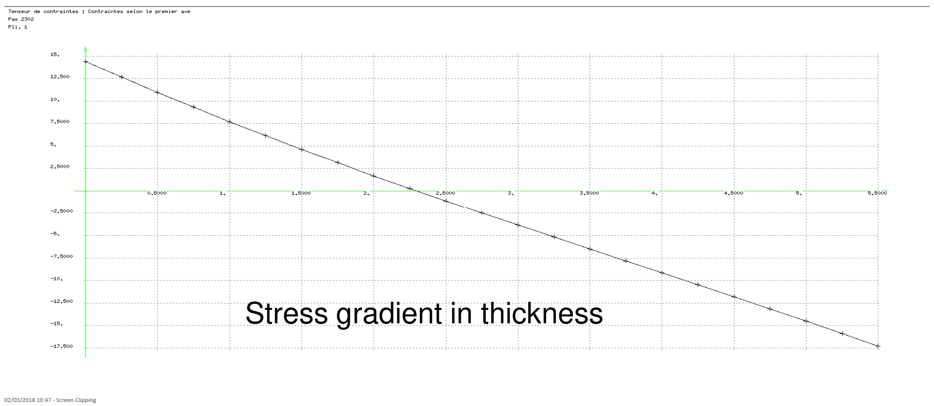
- Simulation of Spring-in without no effect of winding tension



Simulation of conversion degree and Tg for process cycle



Simulation of final x deformation for asymmetric model for mandrel and composite systems



Stress gradient in thickness

- Prediction of spring-in is closed to tests results with DMA tests parameters identification and very under with creep-Compression tests.
- With DMA, viscoelasticity is identified with shearing mode of deformation that are wider than for transverse mode deformation.
- Effects of initial winding tension needs three different values to evaluate only resin effect

Thank you for your attention

Any questions ?

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