

CHARACTERISATION OF AN AERONAUTIC EPOXY RESIN DURING THE MANUFACTURING PROCESS – SIMULATION OF RESIDUAL STRESSES IN EPOXY MATRIX COMPOSITES

Y. Abou Msallem ^{1,4}, F. Jacquemin ¹, N. Boyard ², A. Poitou ¹, D. Delaunay ², and S. Chatel ³

¹ *GeM, Ecole Centrale de Nantes - Université de Nantes, UMR CNRS 6183, France.*

² *LTN, Ecole Polytechnique de l'Université de Nantes, UMR CNRS 6607, France.*

³ *Mechanical Modeling Research Team, EADS France CTO/IW/SP/ME, France.*

⁴ *Corresponding author's E-mail: frederic.jacquemin@univ-nantes.fr*

SUMMARY: A thermal, rheological and mechanical material characterisation of an aeronautic epoxy resin from commercial prepregs is reported in this article. The kinetic of the chemical reaction and the heat capacity are characterized by differential scanning calorimetry (DSC). The thermal conductivity, the thermal expansion coefficients, the volumetric shrinkage, the effective chemical shrinkage coefficient have been identified using a specific mold (named PVT α mold). Dynamic mechanical measurements are used to determine the rheological properties. This rheological study allows estimating the gelation times for different curing temperatures. The degree of reaction at the gel point is found to be independent of the temperature. Finally, the residual stresses are calculated using a finite element simulation and taking into account the material properties evolutions, the temperature and the degree of cure gradients during the curing process. For example, the simulations emphasize the curing residual stresses presented in the composite material before cooling.

KEYWORDS: Material characterisation, finite elements, residual stresses

INTRODUCTION

The use of composite materials is growing rapidly especially for aeronautic structures. The curing of thick composite parts, for example, is a challenging task because it can lead to temperature and degree of polymerization gradients through the thickness. These phenomena are due to the combination between the low thermal conductivity of the composite and the large heat of reaction generated during the crosslinking reaction.

The temperature and degree of cure gradients, the chemical shrinkage, the evolution of properties of the matrix during the curing process and the material anisotropy lead to the development of residual stresses in the manufactured part. These residual stresses can have a significant effect on the mechanical performance of composite structures by initiating cracks or inducing warpage especially for the complex shape parts.

So an appropriate modeling of the kinetic of reaction is essential to simulate the processing of thermosetting materials. Important information to be identified is the glass transition temperature (T_g). The reaction rate becomes near to zero when the temperature is below T_g and the material behavior change from rubbery state to glassy state. In addition, a rheological study is performed to correctly identify the genesis of residual stresses at the gel point. Finally, a finite element approach is used to simulate the residual stresses generated by the curing process.

THERMO-CHEMICAL CHARACTERISATION

Characterization of the Kinetic of Reaction

The reaction kinetics of the resin is characterized with a Pyris-type differential scanning calorimeter. To estimate the degree of polymerization (α) of the resin, it is necessary to know the polymerization rate and the total enthalpy (ΔH) released during the reaction.

The resin cure is modeled by an empirical autocatalytic kinetic equation that describes polymerization rate through a combination of Arrhenius and polynomial functions. The model proposed by Bailleul et al. [1] has been extended to consider the effects of glass transition temperature. In fact, we assume that the Arrhenius relationship and the viscoelastic relaxation rate act in parallel [2, 3]. Eqn. (1) models the polymerization rate:

$$\frac{d\alpha}{dt} = K_A(T) \cdot G(\alpha) \cdot K_{VE}(Tg(\alpha)) \quad (1)$$

where:

- $G(\alpha) = \sum_{i=0}^{i=7} b_i \times \alpha^i$ is a polynomial function obtained by fitting the experimental variation of the polymerization rate with the extent of reaction;
- $K_A(T) = k_{ref} \cdot EXP\left(A\left(\frac{T}{T_{ref}} - 1\right)\right)$ is an Arrhenius function that describes the dependence of the polymerization on temperature.
- $K_{VE}(T) = EXP\left(C_1 \frac{T - T_g(\alpha)}{C_2 + |T - T_g(\alpha)|}\right)$ is an exponential function that describes the influence of the viscoelastic relaxation.

In Fig. 1, comparisons of model predictions with PVT α mold measurements illustrate the accuracy of the model to predict the reaction kinetic for heating ramps and isothermal temperature.

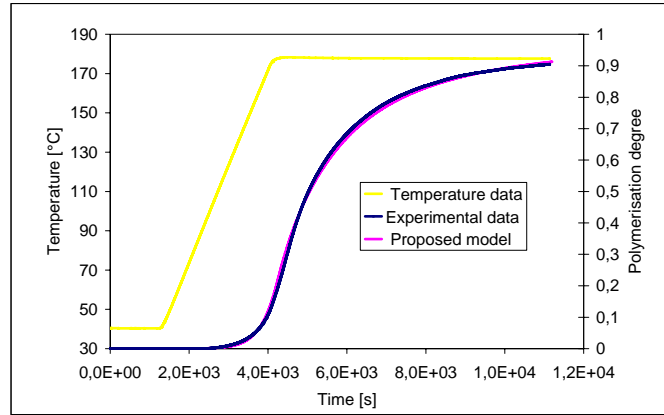


Fig.1 Comparison of the polymerization degree from PVT α mold measurement and proposed model.

Characterization of the Glass Transition Temperature

The glass transition temperature corresponds to a phase change of the material, which has a great influence on the reaction kinetic rate. An experimental method, using the PYRIS DSC, is performed for measuring the variation of this glass transition temperature with cure. This method consists of heating the material sample in the DSC:

- making a heating ramp of 5°C/min up to a constant temperature T,
- maintaining this temperature during a time t inducing partially cured samples,
- decreasing the temperature of the samples to the ambient temperature,
- increasing the temperature by heating ramp of 5°C/min to a temperature insuring that the ultimate degree of cure is reached. At this step, by plotting the variation of the heat flow with temperature, the residual heat enthalpy ΔH_{resid} is determined and then the degree of polymerization (2) is calculated. The glass transition corresponds to a change in the slope of the heating flow.

$$\alpha = 1 - \frac{\Delta H_{resid}}{\Delta H_{tot}} \quad (2)$$

where ΔH_{tot} is the total heat enthalpy.

So by repeating this experience for different isothermal times, we obtain the variation of T_g with cure. The theory assume that the increase in T_g with extent of cure has two sources: reduced free volume from fewer chain ends and reduced segment mobility from crosslinking. In our work, the evolution of T_g is modeled by the relation of Di-Benedetto [4] (3):

$$T_g(\alpha) = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{[1 - (1 - \lambda)\alpha]} \quad (3)$$

$T_{g\infty}$ and T_{g0} are respectively the glass transition temperature for the cured and the uncured resins, λ is a material constant which is determined by using an iterative process based on the least squares method. Now, knowing the variation of the extent of cure and the variation of T_g with α , we can plot the variation of T_g with time (Fig. 2) and the Time-Temperature-Transformation (TTT) diagram of the resin.

Thermal Characterization by Using the PVT α Mold

The changes in specific volume, coefficients of thermal expansion (CTE) and coefficient of chemical shrinkage (CCS) of cured and uncured samples are determined by using the PVT α mold.

This mold allows measuring the temperature, the heat flow, the pressure and the volumetric change of a cylindrical sample placed inside a rubber-made capsule. Being incompressible and having a low modulus the rubber follows the variation of the material sample.

The volumetric change is identified by measuring the displacement through the thickness of the sample (4), assuming that the area of the sample remains constant [5]. In our case, the pressure is constant and hydrostatic, so we consider that the overall change in volume of the material sample is a combination between the volumetric chemical shrinkage and the volumetric thermal variation (4).

$$\frac{\Delta v}{v} = \frac{S \cdot \Delta e}{S \cdot e} = CTE_v \cdot \Delta T + CCS_v \cdot \Delta \alpha \quad (4)$$

where $\frac{\Delta v}{v}$ is the incremental volume change of the resin sample, CCS_v is the volumetric coefficient of chemical shrinkage and CTE_v is the volumetric coefficient of thermal expansion.

Assuming a linear dependence of the CTE_v with the polymerization degree (5), we have to determine the coefficients of the thermal expansion of the cured and uncured resins.

$$CTE_v^{resin} = \alpha CTE_v^{cured} + (1 - \alpha) CTE_v^{uncured} \quad (5)$$

After determining the CTE_v^{resin} of the sample, the variation of the specific volume with the degree of polymerization [5] is deduced by subtracting the thermal part of the volume variation. Assuming a linear variation [6,7], we can determine the coefficient of chemical shrinkage of the resin.

RHEOLOGICAL CHARACTERISATION

Dynamic rheological measurements are performed, with an ARG2 parallel plates Rheometer, at different isotherms. By plotting the loss factor as a function of time for different frequencies (Fig. 3), the gel point corresponds to the intersection of $\tan(\delta)$ curves [8], where $\tan(\delta) = \frac{G''(\omega)}{G'(\omega)}$ and $G'(\omega), G''(\omega)$ are respectively the elastic shear modulus and the viscous shear modulus. At the intersection, $\tan(\delta)$ is equal to 0.6 ± 0.01 ($\neq 1$). It means that viscous modulus and elastic modulus are not equal at this point.

The polymerization degree at the gel point is found to be temperature independent ($\alpha_{\text{gel}} = 0.54 \pm 0.03$). The determination of the variation of the gel time with temperature and the knowledge of the change in glass transition temperature, depending on the degree of polymerization, permits drawing the TTT diagram (Time – Temperature - Transformation) which permits the characterization of the material states.

In conclusion, we have measured the isothermal variation of the transient viscosity and the elastic and viscous shear modulus with time. Knowing the variation of the degree of polymerization with time, we can deduce the variation of these properties with α . Assuming that the Poisson's coefficient is cure independent [7], the variations of E' and E'' are determined for the first stages after the gel point, but in later stages the gel becomes solid and we exceed the rheometer capacities. So, to measure the variation of the mechanical properties, for all the stages of material curing, we use a viscoanalyser permitting the determination of the properties also in the solid phase.

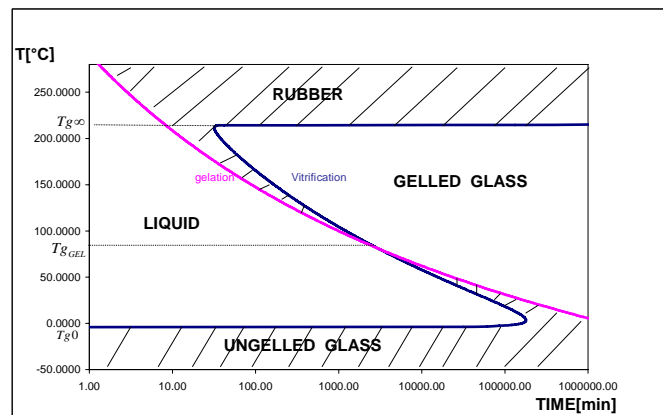


Fig. 2 TTT diagram.

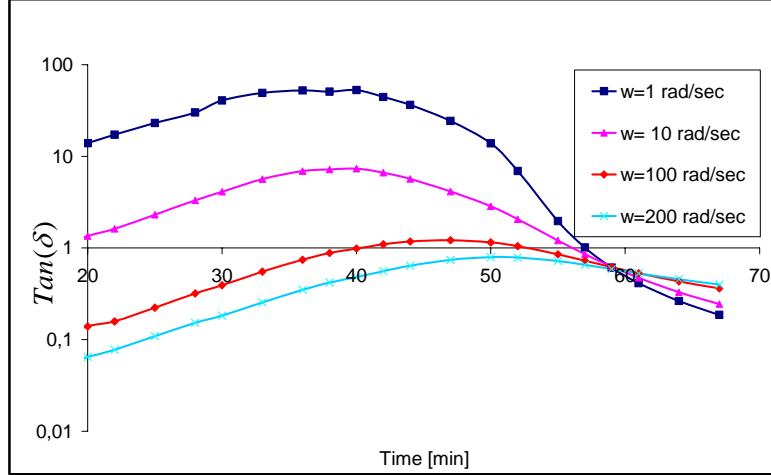


Fig. 3 Loss factor $\tan(\delta)$ as a function of time at different frequencies at 160°C .

THERMO-MECHANICAL CHARACTERISATION

The resin mechanical properties vary with cure. The knowledge of the variation of these properties is essential for the estimation of the residual stresses. Some authors [7] have reported a linear correlation between the degree of polymerization and the mechanical properties. In this work, a dynamic mechanical thermal viscoanalyser (DMTA Metravib VA 2000) is used for the determination of the mechanical properties variations with the temperature and degree of polymerization. Fully cured samples and postgel cured samples (the cure is stop after the gel point) are prepared ($80 \times 10 \times 3 \text{ mm}^3$) with a specific curing cycle for the DMTA measurements. To measure the variation of the elastic modulus of the fully cured and postgel cured samples with temperature, tension tests are performed by increasing the temperature and making isothermal ramps (10 min) ensuring thermal equilibrium. For the postgel cured samples, the temperature is increased until the T_g of partially cured resins.

Our goal is to model the variation of the elastic modulus with α , so we start with a model based on the percolation theory:

$$E'(\alpha) = E'_\infty \left(\frac{p - p_c}{1 - p_c} \right)^{2.7} \quad (6)$$

where E'_∞ is the elastic modulus of the fully cured resin and p is the percolation bond probability [9,10]. In the simplest scheme, the bond probability is equal to the square of the degree of polymerization. In fact this theory is used for the equilibrium modulus (E) but as we know that the elastic modulus is approximately equal to the equilibrium modulus for frequencies sufficiently low ($\omega \ll \tau_z^{-1}$ where τ_z is the longest relaxation time). When T_g is closed to the measurement temperature, the increases of the relaxation times involve that $E' > E$. So, we can model the variation of E' according to the percolation theory if our material is cured isothermally above its glass transition temperature and when the glass transition temperature approach the

cure temperature ($|T - T_g| < 20^\circ K$) this law is not valid because of the effect of the glass transition on the material properties. So we need to model the variation of this elastic modulus with degree of polymerization and glass transition temperature. Eqn. 7 models accurately the variation of the elastic modulus:

$$E'(T, \alpha) = E'_{\text{postgel}}(T) - \left(E'_{\text{cured}}(T) - E'_{\text{postgel}}(T) \right) \left(\frac{\alpha^2 - \alpha_{\text{postgel}}^2}{\alpha_{\text{max}}^2 - \alpha_{\text{postgel}}^2} \right) f(T_g) \quad (7)$$

$$E'_{\text{postgel}}(T) = \sum_{i=0}^{i=3} a_i \times T^i \quad E'_{\text{cured}}(T) = \sum_{i=0}^{i=5} c_i \times T^i$$

$$f(T_g) = C_3 \exp \left(C_4 \frac{T_g(\alpha) - T}{C_5 + |T_g(\alpha) - T|} \right)$$

where α_{postgel} is the degree of the polymerization corresponding to sufficiently important elastic modulus, α_{max} is the maximum degree of polymerization attained ($\alpha_{\text{max}} = 0.97$), E'_{postgel} and E'_{cured} are respectively the modulus at α_{postgel} and α_{max} . Finally, C_3 , C_4 and C_5 are material constants.

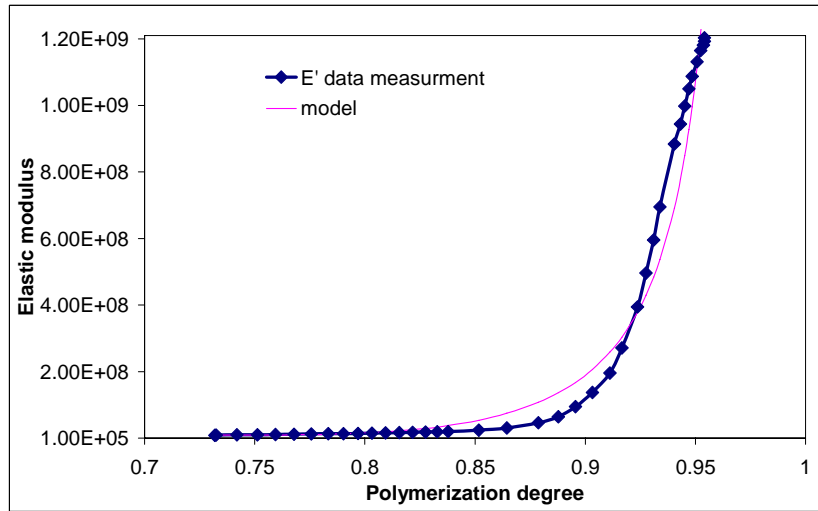


Fig. 4 Elastic modulus comparison from experimental data and proposed model at 180°C.

RESIDUAL STRESSES SIMULATION

A study of process-induced stresses is presented in this section. Lamina properties are highly dependent on the fiber and resin properties, and fiber volume fraction. Properties of the fiber are assumed constant and independent of cure. The instantaneous spatially varying properties in the composite laminates are calculated using a micromechanical model [6, 7].

The methodology for predicting the process-induced residual stresses and corresponding strains is computed with Femlab 3.1i and Matlab by using three modules: heat transfer module coupled with the PDE (Partial Differential Equation) module, for the temperature and degree of polymerization determinations, and a mechanical structures module to calculate the residual stresses and strains.

The cure of a unidirectional rectangular plate ($30 \times 30 \times 1 \text{ cm}^3$) is simulated. The curing cycle is the one proposed by the supplier of material. Fig. 5 shows a comparison of the transverse stress variations, at the centre of the plate during the curing cycle, estimated by using a linear model or our proposed model for representing the mechanical properties. The temperature at the centre is also presented in the same graphic. The proposed approach predicts quasi null transverse stresses before cooling down and less important residual stresses, in comparison with the linear approach, at the ambient temperature.

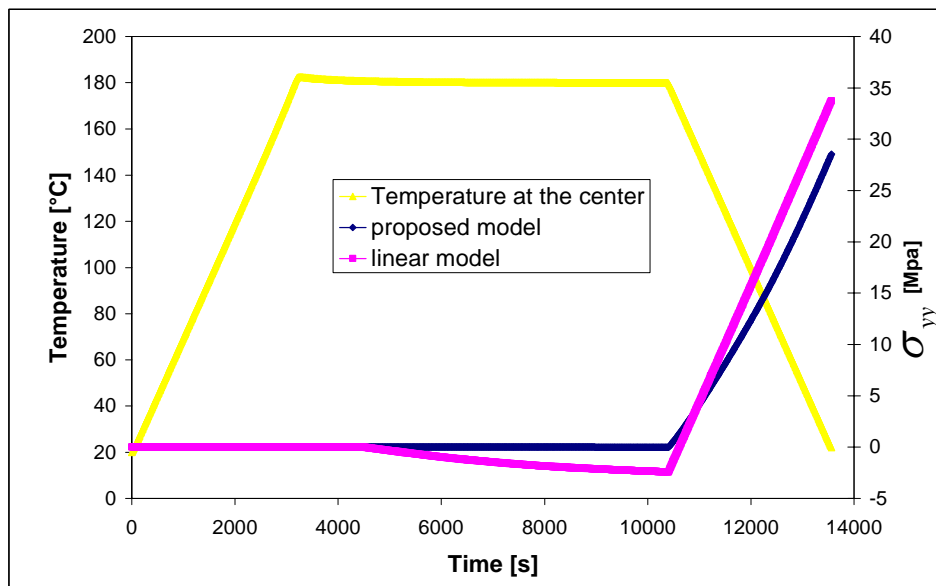


Fig. 5 Transverse residual stresses at the centre of the plate during curing process.

CONCLUSION

A kinetic and rheological characterization of an aeronautic epoxy resin is performed. We have studied the resin properties variations during the curing process. A thermo-chemically-elastic model is used to calculate the in-situ residual stresses by using a finite element code. The importance of taking into account the gel point and thus the residual stresses presented before cool-down is emphasized. A future work will concern the determination of a yield stress for the resin and its dependence on temperature and degree of cure. The knowledge of this characteristic stress state could explain the relaxation of a part of the residual stresses exceeding the yield stress.

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