

Identification of thermal and rheological properties of an aeronautic epoxy resin-simulation of residual stresses

Y. Abou Msallem¹, N. Boyard², F. Jaquemin¹, A. Poitou¹, D. Delaunay², S. Chatel³

¹*GeM, Ecole Centrale de Nantes-Université de Nantes, UMR CNRS 6183, 1 rue de la Noé, 44300 Nantes, France.*

URL: www.ec-nantes.fr

e-mail: youssef.abou-msallem@ec-nantes.fr

²*LTN, UMR 6607, Ecole Polytechnique de l'Université de Nantes, rue Christian Pauc, 44306 Nantes, France.*

³*EADS France, Mechanical Modelling Research Team, 12 rue Pasteur, BP 76, 92162 Suresnes, France.*

ABSTRACT: An extensive material study of an aeronautic epoxy resin from commercial prepregs is reported in this article. The kinetics of the chemical reaction and the heat capacity are characterized by differential scanning calorimetry (DSC). The thermal conductivity, the thermal expansion coefficient, crosslinking heat flux and associated degree of cure, 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. The gel times at different curing temperatures are estimated. The degree of polymerization at the gel point is found to be independent of temperature. Finally, the residual stresses in a composite part are calculated using a finite element simulation and taking into account the evolution of the material properties, the temperature and degree of cure gradients during the curing process.

Keywords: identification, composite materials, finite elements, residual stresses.

1 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 cross-linking polymerisation.

The temperature and degree of cure gradients, the chemical shrinkage, the evolution of properties of 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 modelling of the kinetics of reaction is essential to simulate the processing of thermosetting materials. Another important phenomenon 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 behaviour change from rubbery to glassy state. In addition, a rheological study is lead 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.

2 CHARACTERISATION

The specific heat, the reaction kinetics and the glass transition temperature of the resin are characterised with a differential scanning calorimeter of the PYRIS type.

2.1 The reaction kinetics

The relation between the degree of polymerisation (α) of the resin, and the polymerisation rate ($d\alpha/dt$) is obtained by the classical method based on the partial area under the peak. ΔH the total enthalpy of polymerisation is the total area under the peak. A

sigmoid is used for the base line.

An endothermic peak was observed on the heat flow curves. This peak is due to the melting of thermoplastic nodules. It is suppressed on figure 1.

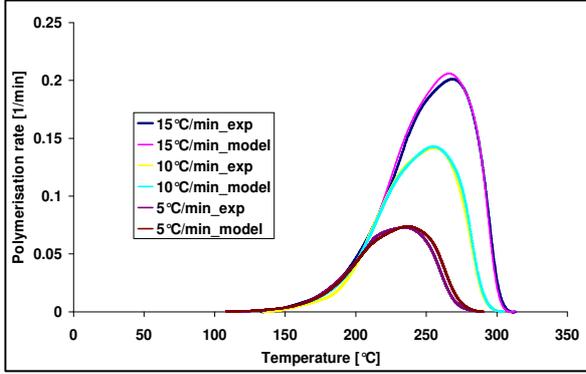


Fig. 1. DSC measurement of the reaction rate and prediction of the proposed kinetic model.

In this paper, resin cure is modelled by an empirical autocatalytic kinetic equation which describes polymerisation through a combination of Arrhenius and polynomial functions. The model proposed by Bailleul [1] has been extended to consider the effects of glass transition temperature:

$$\frac{d\alpha}{dt} = \begin{cases} K(T).G(\alpha) & \text{if } T > T_g \\ 0 & \text{if } T < T_g \end{cases} \quad G(\alpha) = \sum_{i=0}^{i=7} b_i \times \alpha^i,$$

$$\text{and } K(T) = K_{ref} \cdot \text{EXP}\left(-A\left(\frac{T_{Ref}}{T} - 1\right)\right)$$

In figure 1, comparisons of model predictions with DSC measurements illustrate the accuracy of the model to predict the reaction rate for different heating rates.

2.2 The specific heat

The dependence of the thermal capacity on temperature and degree of polymerisation can be modelled by the following form:

$$Cp_{resin}(\alpha, T) = \alpha.Cp_{cured}(T) + (1-\alpha).Cp_{uncured}(T)$$

$$Cp_{cured} = 0.004608.T + 1.1$$

$$Cp_{uncured} = 0.0016.T + 1.6421 \quad (\text{J/g}^\circ\text{C})$$

Then, the problem is reduced to the determination of specific heats of the cured and uncured resins. For the cured resin, the melting point (190 °C) of thermoplastic nodules makes difficult an accurate analysis of the results. However, we can find an average for the specific heat for temperatures below

180 ° C.

2.3 The glass transition temperature

The glass transition temperature corresponds to a phase change of the material. The $T_g(\alpha)$ relation is integrant part of the kinetics.

The dependence of T_g on the degree of polymerisation (figure 2) is modelled by the relation

$$\text{of Di Benedetto [2]: } \frac{(T_g - T_{g0})}{(T_\infty - T_{g0})} = \frac{\lambda.\alpha}{[1 - (1-\lambda).\alpha]}$$

with $T_{g0} = -4.15^\circ\text{C}$, $T_{g\infty} = 215^\circ\text{C}$ and $\lambda = 0.551$

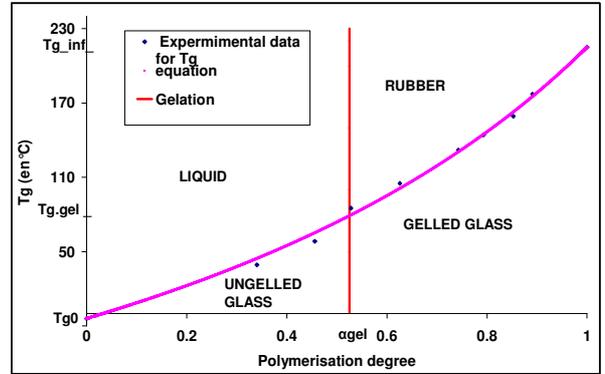


Fig. 2. CTT diagram showing resin gelation and vitrification.

3 CHARACTERISATION BY USING THE PVT α MOLD

The PVT α mold allows measuring simultaneously the heat flow, the temperature, the pressure and the volumetric change on a cylindrical sample [3].

3.1 Heat conductivity

Two types of approaches are performed to measure the conductivity: the method of the guarded hot plate and the PVT α mold. The conductivity is modelled as a linear function of the polymerisation degree (1). We note a small decrease in the conductivity as the temperature approaches the glass transition temperature of thermoplastic nodules. The average conductivities for uncured and cured resins are:

$$\lambda_{uncured} = 0.15 \quad \text{and} \quad \lambda_{cured} = 0.23 \quad (\text{W/m } ^\circ\text{K})$$

and:

$$\lambda_{resin}(\alpha, T) = \alpha.\lambda_{cured} + (1-\alpha).\lambda_{uncured} \quad (1)$$

3.2 The volumetric shrinkage

The thickness of the moulding cavity in which the sample is placed inside a rubber made container is measured by the PVT α apparatus. Being incompressible and having a low modulus, the rubber follows the shrinkage of the resin and fills the volume of the mould, acting like a liquid. In this case, we can determine the total specific volume shrinkage of the completely cured resin: $v_{sh}^T = 6\%$.

3.2.a Coefficient of thermal expansion

The coefficients of thermal expansion (CTE) of cured and uncured samples have been determined by assuming a linear relation between the temperature and the resin specific volume. A linear model as a function of degree of polymerisation can be written:

$$CTE_{resin}(\alpha, T) = (1 - \alpha).CTE_{uncured} + \alpha.CTE_{cured}$$

$$CTE_{uncured} = 5.4 \cdot 10^{-4} \text{ } ^\circ\text{C}^{-1} \quad CTE_{cured} = 5.976 \cdot 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

3.2.b Coefficient of chemical shrinkage

By assuming a linear variation of the volume change with the degree of polymerisation shown in [3], we can determine the coefficient of chemical shrinkage of the resin, which is about 0.02.

4 RHEOLOGICAL CHARACTERISATION

Dynamic rheological measurements are performed, with an ARG2 parallel plates Rheometer, at different isotherms. By plotting the loss factor $\tan(\delta) = \frac{G''(\omega)}{G'(\omega)}$ as a function of time for different frequencies (fig. 3), the gel point corresponds to the intersection of $\tan(\delta)$ curves [4].

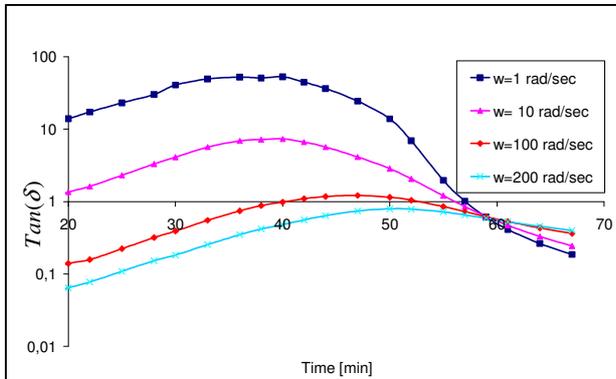


Fig. 3. Loss factor $\tan(\delta)$ as a function of time at different frequencies at 160 °C.

It is difficult to observe this crossover for temperatures above 190°C (melting temperature of thermoplastic nodules). $\tan(\delta)$, at 160 °C, is equal

to 0.6 ± 0.01 ($\neq 1$). It means that viscous modulus $G''(\omega)$ and elastic modulus $G'(\omega)$ are not equal at this point. The figure 4 shows the gel time as a function of temperature. The polymerisation degree at the gel point is temperature independent ($\alpha_{gel} = 0.525 \pm 0.005$).

With the determination of the gel point and the knowledge of the change in glass transition temperature, depending on the degree of polymerisation, we can draw the CTT diagram (Conversion – Temperature - Transformation) which permits the characterisation of the material states (figure 2).

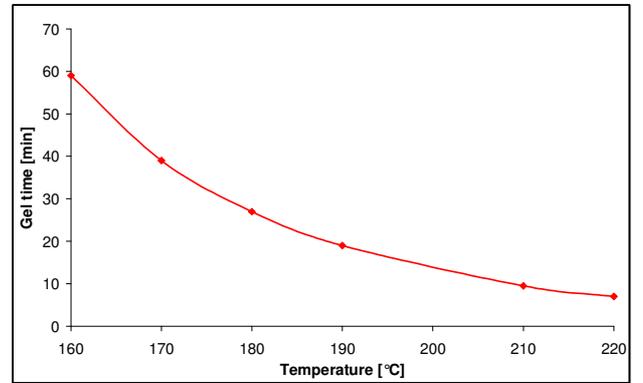


Fig. 4. Gel time measured data versus temperature.

5 RESIDUAL STRESSES SIMULATION

A study of process-induced stresses is presented in this section. Lamina properties are highly dependent on the fiber and resin constituent properties, and fiber volume fraction. Properties of the fiber are assumed constant and independent of cure. The mechanical properties of the resin vary according to a material model based on percolation theory [5].

The instantaneous spatially varying properties, within the composite laminates are calculated using a micromechanical model [6].

The methodology for predicting the process-induced residual stresses and corresponding strains is coded into 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 polymerisation determinations, and a mechanical structures module to calculate the residual stresses and strains:

$$\bar{\sigma} = \bar{C}(\alpha) \left(\bar{\varepsilon} - \bar{\beta}(\alpha) \Delta T - \bar{\chi}(\alpha) \Delta \alpha \right)$$

Where $\overline{\sigma}$ is the stress tensor, $\overline{C}(\alpha)$ is the rigidity tensor, $\overline{\varepsilon}$ is the strain tensor, $\overline{\beta}(\alpha)$ et $\overline{\chi}(\alpha)$ are the thermal expansion and the chemical shrinkage tensors. The curing 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. Figure 5 shows the temperature and degree of polymerisation variations at the centre of the plate. The reaction being exothermal, the temperature in the middle of the sample becomes higher than the one imposed by the thermal cycle.

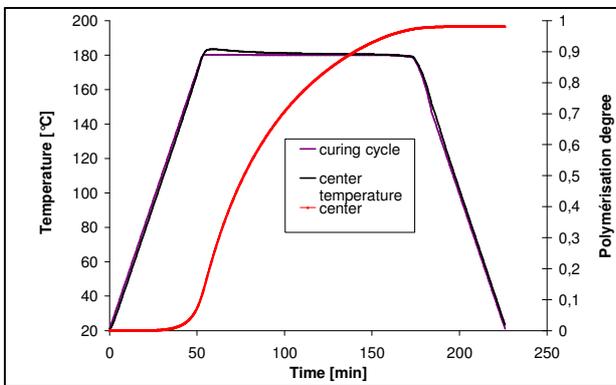


Fig.5. Numerical calculation of temperature and degree of polymerisation at the centre of the plate.

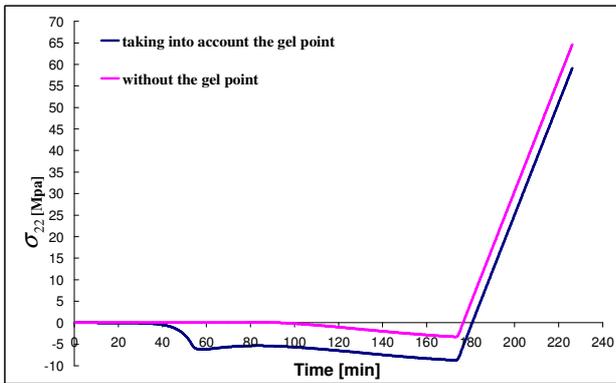


Fig. 6. Computed transverse residual stresses at the centre of the plate during curing process.

The transverse plane stresses at the centre of the plate as a function of time are shown in figure 6. The simulations emphasize the curing residual stresses presented in the composite material before cooling. We can see the important role of the gel point for the

prediction of the residual stresses.

We can also see that the exothermic reaction causes at the centre of the plate a compressive stress state in the middle of the piece that turns into traction stress state during the cooling phase.

6 CONCLUSIONS

A kinetic and rheological characterisation 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 his 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.

REFERENCES

1. J.L. Bailleul, D.Delaunay, Y. Jarny, "Determination of temperature variable properties of composite materials: methodology and experimental results", Journal of reinforced plastics and composites, 1996, Vol.15, p. 480-496.
2. J.P. Pascault, H. Sautereau, J. Verdu, R.J.J. Williams, "Thermosetting Polymers". Fourth edition 2002, Marcel Dekker, Inc.
3. N.Boyard, A. Millischer, V. Sobotka, J.L.Bailleul, D.Delaunay,"Behaviour of a moulded composite part. Modelling of dilatometric curve (constant pressure) or pressure (constant volume) with temperature and conversion degree gradients", Composite Science and Technology, 2007, vol. 67, pp. 943-954.
4. H. Winter, "Can the gel point of cross linking polymer be detected by the G'-G'' crossover". Polymer Engineering and science, 1987, Vol. 27, p. 1698-1702.
5. D.B. Adolf, R.S. Chambers, "A thermodynamically consistent, nonlinear viscoelastic approach for modelling thermosets during cure". Journal of Rheology, 2007, Vol. 51, p. 23-50.
6. T.A. Boggetti, J.W. Gillespie, "Process-Induced Stress and Deformation in Thick-section Thermoset Composite Laminates". Journal of Composites Materials, 1992, Vol. 26, p. 626-660.