

FEM SIMULATION OF A THERMOSETTING EPOXY MATRIX: APPLICATION TO INTERNAL STRESSES

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Abstract

A novel approach has been developed to simulate internal stress growth during the curing of thermosetting systems. Couplings between the thermal, the chemistry and the mechanics were taken into account. Especially, heat produced by the thermosetting reaction was considered for the cure kinetics simulation. As a consequence, chemical shrinkage and thermal properties evolutions during the curing were obtained from the degree of cure computed at each time of the curing. Mechanical characteristics evolution with temperature and degree of conversion of the chemical reaction were deduced from DMA-TMA experiments. The numerical solving of the coupling problem was performed with the finite element software Abaqus.

Simulation results for internal stress developments were validated by failure prediction for the Pyrex test tube containing the resin as observed experimentally. It confirms the validity of the FEM model for cure simulation and internal stress prediction.

1 Introduction

The use of composites in structural applications has become increasingly important in the industry. These trends have recently emerged in naval construction since the optimization of the structures became inevitable. Such use requires a highly accurate knowledge of material properties and of the internal state obtained at the end of the manufacturing process.

This is crucial during the curing of the matrix of a carbon-epoxy laminate where internal stresses and defects are generated. They are resulting from a complex process where the thermal, the chemistry, the physics and the mechanical phenomena are

involved. It is strategic for the designers to have an accurate description of the internal state of the material obtained at the end of the curing in order to predict an efficient service life of the structure by using stress based criteria. This acknowledgement is especially the case for thick thermosetting composites (actually more than 5 mm thick)

For example, internal stresses are generated and several imperfections (bubbles, cracks, fiber waviness...) may appear during the curing of a composite, thus decreasing the mechanical performance of the final material. In thin composites, the phenomenon of fiber waviness also seems to be active as suggested by the study of Paluch [1] into long carbon fibers. This author clearly showed that the fibers assume an undulatory form at the end of the cure.

Unfortunately, it has been shown in practice that fiber undulation or waviness has a negative influence on the stiffness and strength of fiber-reinforced composites [2]. Several modeling approaches were used in order to determine this loss of strength. The quality of the predictions depends on the initial value of the wavelength and amplitude of the fiber, which results from the cure process. Currently, no study exists for the prediction of a complete microscopic stress-strain distribution inside a composite after its cure. Existing models only solve the macroscopic strengthening of a composite, either by means of a parametric study of the description of fiber defects, kink band approaches, or the spectral density of waviness. The literature does not take the behavior of the matrix during the cure, fiber-matrix interaction and its consequences on the stress state of the matrix after the return to room temperature into account. Only the cooling step for the return at room temperature seems to have been studied in the literature.

However, previous studies resulting from collaboration between the ENSIETA and the

ENSMA graduate schools of engineering have shown that the gelation reaction is also a source of internal stress creation. Indeed, the resin shrinks strongly during the curing and at the same time its elasticity is developed. Stress setup generated by the gelation reaction of the cure cycle was presented by real-time monitoring of the undulation and description of a T300 carbon fiber embedded in LY556 epoxy resin [3].

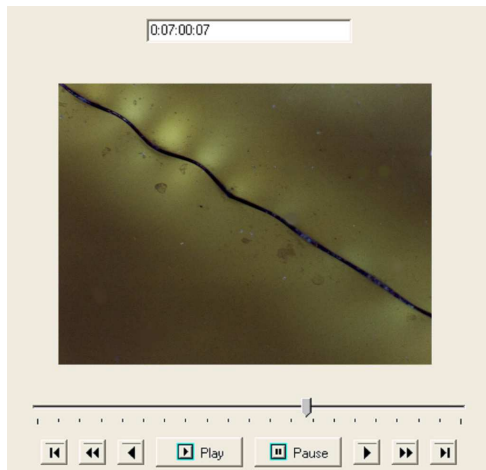


Fig. 1. T300 carbon fiber undulations observed by video records

The chemical shrinkage generates a compressive load to the fiber and under this action the fiber buckles.

These works provided a better understanding of the mechanisms of fiber microbuckling, but they especially have shown the necessity to take into consideration the complete cure cycle in order to quantify internal stresses generated by the curing.

The curing of a thermosetting matrix results from a complex process where thermal, physicochemical, viscosity and mechanical phenomena are mixed. This complexity is increased by the thermo activated and exothermal behaviors of the thermosetting chemical reaction of the resin. Moreover throughout the cure, mechanical characteristics are evolving with temperature and degree of conversion of the chemical reaction. Tools using advanced finite elements made their appearance. However these tools are established on formulations where all the couplings are not taken into account. The modeling of these phenomena coupled with the temperature and with the mechanics seems to be never having been approached previously.

Thus, the aim of this research is to build up a simulation tool for the process of cure, based on a coupling model taking into account the mechanics, the thermal, the diffusion and the chemistry. This is a strategic way to understand internal stress mechanism appearing during the cure. It should lead to a better description of material characteristics gradients present at the end of cure and namely the internal residual stress state obtained. Therefore, in the next chapter of the presentation a coupling model between the chemistry, the thermal and the mechanics is exposed. The couplings taken into consideration concern the shrinkage induced by the thermosetting reaction and the corresponding heat generated. This lead to the determination of the cure kinetics and hence mechanical behavior of the resin can be described by an elastic constitutive law depending on the degree of cure. The third part of the paper presents the numerical setting of the coupling model with the finite elements modeling software Abaqus. A first validation of internal stress development is obtained by failure prediction for the Pyrex test tube containing the resin as observed experimentally.

2 The thermo-chemical and mechanical coupling model

The chemical problem of the thermosetting reaction has to be studied and therefore reactive blend evolution is described by degree of conversion also called degree of cure and usually denoted by α . This parameter α is governed by a time derivative equation with temperature dependent parameters. However, the curing is also an exothermal reaction. Heat produced by the reaction helps to its activation. Hence, a coupling between the thermal and the chemistry exists and it can be described by a heat flow equation whose simplified expression can be written as (Golay, 1991, Jugla, 2005 without diffusion members).

$$\rho C_p \frac{dT}{dt} = - \text{div}\{\lambda_T [-\vec{grad} T]\} + f_v + \rho \Delta H^f \frac{d\alpha}{dt} - T \{(3\lambda + 2\mu) \alpha_T\} \text{tr} \underline{\underline{\epsilon}}^e \quad (1)$$

where C_p stands for specific heat, λ_T stands for thermal conductivity, λ and μ are the Lamé coefficients and α_T is the coefficient of thermal expansion of the matrix in formation. f_v stands for the heat flow imposed by the oven and $\rho \Delta H^f \frac{d\alpha}{dt}$ stands for the heat flow produced by the chemical reaction.

Note that the solving of heat equation (1), associated to a progressive material, requires evolution laws for its corresponding material parameters since at each time a matrix is developed with different properties.

Nevertheless, the thermo hardening of an epoxy resin belongs to a phase change from a liquid state to a solid state which is characterized by an associated volume shrinkage also called chemical shrinkage. The curing must therefore be considered as a coupling problem between the thermal, the chemistry and the mechanics. Hence, internal stresses depending on degree of cure and temperature will be generated by the curing.

Thus, in following subsections, a first proposal for material parameters evolution laws during the curing is presented. Elastic progressive behavior of the matrix in formation was analyzed by Dynamical, Mechanical and Thermal Analysis (DMA-TMA visco analyzer).

2.1 Cure kinetics

Differential scanning calorimetric tests (DSC) were performed on a LY556 epoxy blend. The Kamal and Souror model [4] was chosen for the degree of cure modeling. This model given by equation (2) is the most common one in the literature and fits well for autocatalytic kinetics like those of epoxies.

$$d\alpha/dt = (K_1 + K_2 \alpha^m)(1-\alpha)^n \quad (2)$$

$K_1 = a_1 \exp(-e_1/T)$ and $K_2 = a_2 \exp(-e_2/T)$. Table 1 presents Kamal and Sourour corresponding coefficients for the LY556 epoxy blend, obtained by DSC analysis.

Table 1 Kamal and Sourour cure kinetics coefficients for the LY556 epoxy resin system

m	0.75	a ₁	1.41093 10 ³ s ⁻¹	e ₁	5917.89 °K
n	1.25	a ₂	2.35865434 10 ⁶ s ⁻¹	e ₂	7983.42 °K

2.2 Chemical shrinkage

Information for chemical shrinkage developed by the curing of an epoxy matrix is not very common in the literature. Some information about shrinkage is given by resin manufacturers, but this information usually concern the final shrinkage observed at the end of the curing. Recently, in-situ chemical shrinkage of epoxy resins was examined

by Li et al. [5], which established a bilinear relationship for cure shrinkage versus degree of cure, with a break point at gelation. As Li et al. demonstrated that neither the degree of conversion rate nor the isothermal level of the curing did affect the bilinear evolution of chemical shrinkage, it was decided to use this modeling of the chemical shrinkage description. Thus, it is assumed that this can be relevant to non isothermal curing and applicable for the LY556 epoxy system. The comparison of the Li et al. shrinkage model with experimental data provided by the LY556 epoxy manufacturer for an isothermal curing at 120°C is shown in Figure 2.

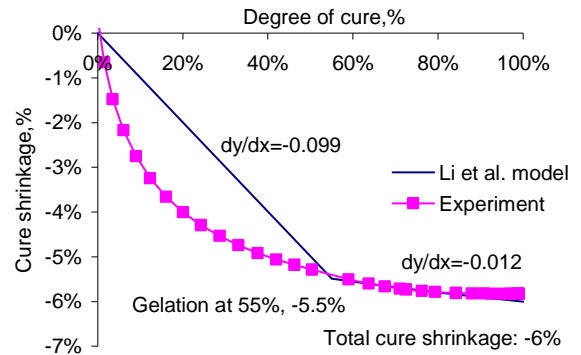


Fig. 2. Chemical shrinkage evolution versus degree of cure for the LY556 epoxy resin estimated by the Li et al. model

2.3 Matrix thermal strain estimation during the curing

Matrix temperature is variable and non uniform during the curing. This heterogeneous temperature field generates expansion or shrinkage. An additional difficulty is linked to the fact the curing of the resin is related to a different and progressive material at each time. One way to solve this difficulty is to consider the chemical blend as a mix of resin and matrix weighted by the degree of cure. In this context, at each time, thermal volume strain evolution for a temperature increment ΔT can be expressed by following linear relation where α_T stands for the thermal expansion coefficient of the mix.

$$d\epsilon_{thermal}^{Vol}(t) = \alpha_T(t) \Delta T \quad (3)$$

Coefficient α_T(t) is defined by α_T(t) = [1 - α(t)] α_{T liquid epoxy} + α(t) α_{T solid epoxy}(t).

$\alpha_{T \text{ liquid epoxy}}$ denotes the thermal expansion coefficient per unit volume for the epoxy resin in its liquid state before gelation and $\alpha_{T \text{ solid epoxy}}$ denotes the thermal expansion coefficient per unit volume for the fully cured epoxy matrix. However, for amorphous polymers, like epoxies, $\alpha_{T \text{ solid epoxy}}$ is temperature dependant and glass transition dependant. Identification of thermal expansion coefficients for the LY556 epoxy system was performed by DMA-TMA analysis. Thus, $\alpha_{T \text{ liquid epoxy}} = 5^{E-4} \text{ } ^\circ\text{C}^{-1}$ and $\alpha_{T \text{ solid epoxy}} = 450^{E-6} \text{ } ^\circ\text{C}^{-1}$ for a vitrous matrix (below glass transition temperature T_g) and $\alpha_{T \text{ solid epoxy}} = 450^{E-6} + 4.1^{E-6} (T-T_g)$ for a rubbery matrix (above T_g).

This modelling requires T_g determination at each time of the curing. T_g was calculated by the usual Pascault and Williams [6] relation (also called Di-Benedetto equation) as follow:

$$\frac{(T_g - T_{g0}) / (T_{g \text{ infinity}} - T_{g0})}{\lambda \alpha / [1 - (1 - \lambda) \alpha]} = \quad (4)$$

where λ is an adjustable, structure-dependent parameter, which ranged between 0.46 and 0.58 for several amine epoxy systems. T_{g0} (T_g at $\alpha = 0$) is the lower limit temperature for the start of the thermosetting reaction of the epoxy blend that stays below T_{g0} in a glassy state. $T_{g \text{ infinity}}$ must be viewed as an estimated value for an idealized fully cured network, physically unachievable. For the LY 556 epoxy system, values obtained are respectively $T_{g0} = 50^\circ\text{C}$; $T_{g \text{ infinity}} = 160^\circ\text{C}$ and $\lambda = 0.46$

2.3 Specific heat Cp (J/gK)

An easy way for the description of the epoxy matrix specific heat evolution is to consider that it can be described by a linear mixture rule relation, weighted by the degree of cure, between the liquid state (resin) and the solid state (matrix), as given by equation (5) :

$$C_p(\alpha, T) = (1-\alpha) C_p(0, T) + \alpha C_p(1, T) \quad (5)$$

where $C_p(0, T)$ and $C_p(1, T)$ stand for liquid resin and fully cured matrix temperature dependant specific heat evolutions. Specific heat expressions established by Bailleul [7] for a similar m10 epoxy system were employed according to the lack of exact value for the LY 556 epoxy system.

2.4 Thermal conductivity λ (W/mK)

In the same manner as previously, thermal conductivity can be easily expressed by a linear mixture rule relation as follow:

$$\lambda(\alpha, T) = (1-\alpha) \lambda(0, T) + \alpha \lambda(1, T) \quad (6)$$

where $\lambda(0, T)$ and $\lambda(1, T)$ stand for liquid resin and fully cured matrix temperature dependant thermal conductivity evolutions. The thermal conductivity for the liquid LY556 epoxy resin was estimated at 0.255 w/mk by Moisala [8]. Temperature dependency of the thermal conductivity of the LY556 resin was then assumed to be in the same way as those established by Bailleul for the m10 epoxy system.

2.5 Heat flow of the thermosetting chemical reaction (W/m3)

As defined by the DSC analysis, the heat flow $\phi(t)$ produced by the chemical reaction associated to the curing of a thermosetting resin is a linear function of the rate of degree of cure with a slope corresponding to the enthalpy variation ΔH^r of the reaction (equation 7):

$$\phi(t) = \rho \Delta H^r d\alpha/dt \quad (7)$$

Mass enthalpy ΔH^r depends on the temperature at which the reaction is done. This temperature dependency is usually described by a Kirchhoff law and was identified by DSC analysis for the LY556 epoxy system.

2.6 Mechanical behavior

Elastic shear modulus evolution versus degree of cure ($G'(\alpha)$) was carried out by DMA analysis for a 120°C isothermal curing. Bulk modulus evolution versus degree of cure ($K(\alpha)$) was estimated by a mixture rule relation between 3 GPa. for the liquid state and 6.3 Gpa. for the solid state (Pascault et al., 2002). Thus, elastic constitutive equation was written as follow:

$$\sigma(t) = [K(\alpha) - \frac{2}{3} G'(\alpha)] \text{tr}(\epsilon(t)) \cdot I + 2G'\epsilon(t) \quad (8)$$

3 FEM simulation

The cure simulation model is applied to the curing of an LY556 Ciba-Geigy epoxy resin. Finite element analysis was performed with the industrial finite element software Abaqus® V. 6.51. From a technical point of view, the solving of equation of heat (1) coupled with the thermal, the cure kinetics (equation (2)) and the production of heat of the thermosetting reaction (equation (7)) were developed with a user material subroutine of Abaqus

(umat), hence allowing the study of real 3D composite structures. Aims of the simulation are to solve the coupling problem on one hand, and on the other hand a parametric study can be performed to check the impact of each coupling on chemical and thermal strain mechanisms and hence internal stress development.

Evolution laws for the coupling between the thermal, the chemistry and the mechanics have highlighted a dependency on three variables: temperature, degree of cure and rate of degree of cure. Coupling of specific heat and thermal conductivity with these three variables were introduced by a tabular form in the Abaqus finite element software. Cure kinetics equation was solved inside of the umat subroutine by an Euler explicit method. The time increment was provided by the Abaqus solving program and its maximum value was fixed according to the maximum time increment allowed for the explicit solving of cure kinetics. By the way, chemical and thermal strain increments were deduced.

4 Results

This section presents simulation results for the curing of the LY556 epoxy resin. The quality of the simulation was first checked for its accuracy concerning the thermal and chemical coupling problem. Thus, internal temperature prediction was compared with thermocouple records done in the center point of the matrix during its curing.

The second part of this section presents simulation results concerning internal stress estimation developed by the curing.

4.1 Thermal and chemical coupling results: local temperature simulation

The curing was experimented in collaboration with the IFREMER institute (French Research Institute for Exploitation of the Sea). A Pyrex test tube with a diameter of 20 mm filled with epoxy resin for a height of 25 mm was placed in an oven and heated with a 3°C/min ramp followed by an isothermal plateau at 120°C. The temperature evolution in the centre of the resin was recorded during the curing. A strong exothermal effect was observed with a peak at around 250°C. This experimental curing was simulated by using the methodology exposed in this paper and results obtained are exposed in Figure 3.

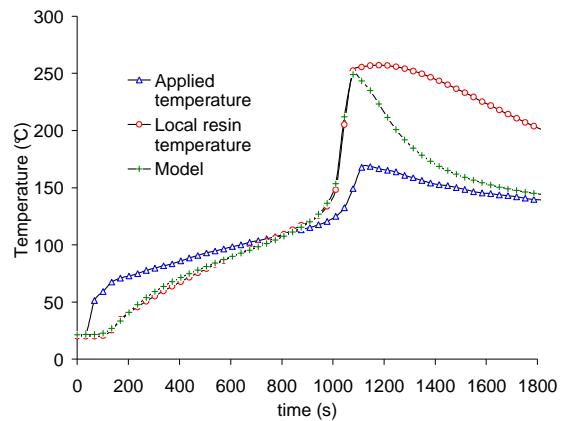


Fig. 3. Local temperature simulation in the centre of the resin (120°C isothermal curing)

Prediction for local temperature evolution is very satisfying except for the decrease of the exothermal peak that is done to quickly. This difference is related to heat exchanges between the matrix and the air above the Pyrex test tube that was not taken into account for the simulation. Moreover, thermal gradients are developed during the curing and are estimated by the model as indicated in Figure 4.

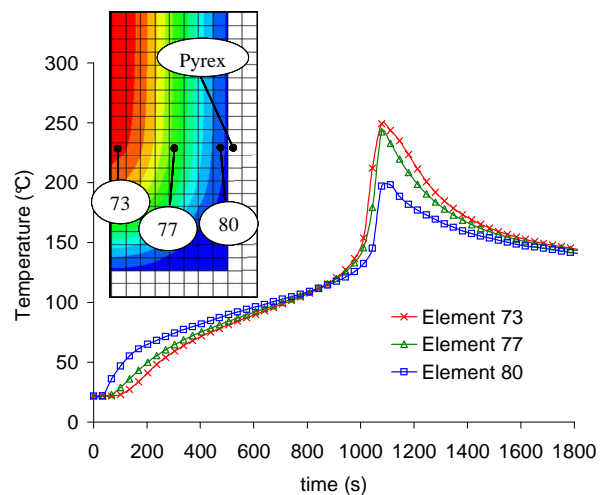


Fig. 4. Thermal gradients developed during the curing of the LY556 epoxy resin

These thermal gradients lead to gradients of degree of cure and hence gradients of strains. This is one of the basic mechanisms for internal stress development during the curing. A first estimation of internal stress, in the framework of elasticity, is proposed in next subsection.

4.2 Thermal, chemical and mechanical coupling results: internal stress prediction

The elastic constitutive law of the matrix in formation is determined by the local degree of cure information as indicated by equation (8) and elastic analysis of the epoxy Pyrex test tube structure leads to a first estimation of the internal stress field developed by the curing as exposed in Figure 5.

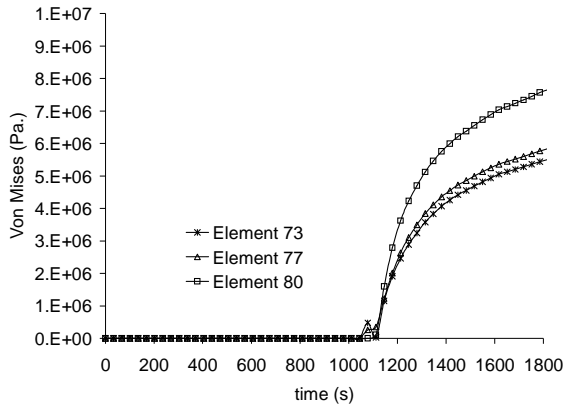


Fig. 5 Von Mises internal stress

Moreover, a first validation of the stress level estimation could be provided by the stress estimation applied on the Pyrex test tube. Indeed, cracks propagations on the test tube walls were observed experimentally during the curing. As indicated in Figure 6 stress level calculated for the Pyrex test tube is much higher than the failure stress for Pyrex.

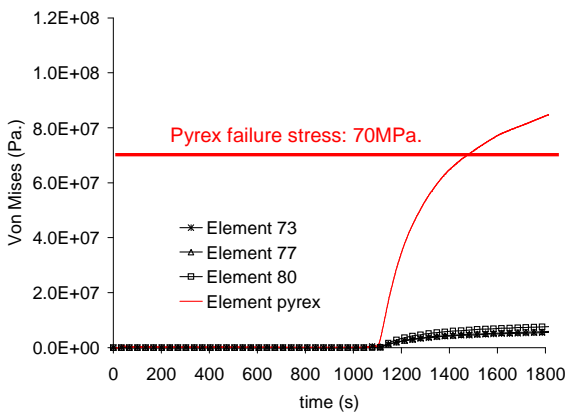


Fig. 6 Von Mises stress evolution of for Pyrex test tube

Strong strain and stress gradients are observed inside of the matrix in formation. In particular, around 7-8 MPa. are obtained after gelation start (from 1000 s). This is an important result providing confirmation of considerable internal stress development during the curing.

5 Conclusion

A Finite element modeling approach has been developed to understand internal stress mechanism appearing during the curing. Hence, a numerical tool coupling mechanical, physical and chemical phenomena was presented and implemented into an industrial FEM code. First results presented in this paper are very positive and made the demonstration of the applicability of finite element modeling approach to provide local information during the curing for real composites structures. The curing of thermosetting systems develops strong thermal gradient inducing therefore residual stresses at the return at room temperature. These stresses are resulting from differential thermal and chemical strains that appear within the material due to gradients of curing generated by thermal heterogeneity.

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