

A FINITE ELEMENT COUPLING MODEL FOR INTERNAL STRESS PREDICTION DURING THE CURING OF THICK EPOXY COMPOSITES

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SUMMARY: 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. Material characteristics evolutions with temperature and degree of conversion of the chemical reaction were deduced from DMA-TMA and MDSC 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.

KEYWORDS: Finite Element Method (FEM), curing, epoxy, couplings, internal stress

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 result from a complex process involving thermal, chemical, physical and mechanical phenomena. It is strategic for designers to have an accurate description of the internal state of the material at the end of cure in order to predict an efficient service life of the structure based on stress failure 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 like bubbles, cracks and namely fiber waviness may appear

during the curing of a composite, thus decreasing the mechanical performance of the final material.

It has been shown in practice that fiber waviness has a negative influence on the stiffness and strength of fiber-reinforced composites [1]. 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 into account 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. Only the cooling step for the return at room temperature seems to have been studied in the literature.

Combined thermal, physicochemical, viscosity and mechanical phenomena occur during the curing of a thermosetting matrix. This complexity is increased by the thermal activation and exothermal behavior of the thermosetting reaction of the resin. Moreover throughout the cure, material properties 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 mechanical laws does not seem to have been considered previously.

The aim of this research is therefore to build up a simulation tool for cure processing, 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. The coupling between the thermal and the chemistry lead to the cure kinetics determination and is presented in the next chapter. Thus, as a consequence, material characteristics can be described as a function of degree of cure and temperature. Mechanical behavior of the resin was modeled by a first simple elastic constitutive law depending on the degree of cure only. The numerical setting of the coupling model with the finite elements modeling software Abaqus were presented in a previous work [2] and results obtained are exposed and discussed in the last section of this paper. A validation of the model was obtained by internal temperature prediction throughout the curing that fits well with the experiment. First prediction for the development of internal stress level gave encouraging results since it predicted the collapse observed on a Pyrex test tube used for the experiment.

THERMO-CHEMICAL AND MECHANICAL COUPLING MODEL

The reactive blend evolution is described by the degree of conversion of the chemical reaction 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 and the heat produced by the reaction helps to its activation. A coupling

between the thermal and the chemistry exits and can be illustrated by the heat flow equation whose simplified expression can be written as (without diffusion members):

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

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, $\rho \Delta H^r \frac{d\alpha}{dt}$ stands for the heat flow produced by the chemical reaction and $\frac{d\alpha}{dt}$ is the rate of conversion.

Note that the solving of heat Eqn. (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. The curing must therefore be considered as a coupling problem between the thermal, the chemistry and the mechanics and a first proposal for material parameters evolution laws during the curing is presented in next subsections. Nevertheless, the thermal hardening of an epoxy resin belongs to a phase change from a liquid 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.

Cure Kinetics

Differential scanning calorimeter (Mettler Toledo TA3000 ME-701776 DSC instrument) tests were performed for the curing of an anhydride epoxy. This epoxy blend consisted of a bifunctional DGEBA-type epoxy (LY556, EEW = 183-192 g/eq, $n = 0.3$), a tetra-functional anhydride hardener (methyl-tetrahydrophthalic anhydride HY917, anhydride equivalent weight = 166g/eq), and an accelerator (1-methyl imidazole DY070). The components were mixed in LY556/HY917/DY070 weight ratio of 100/90/1, resulting in a stoichiometric epoxy-anhydride mixture. The phenomenological Kamal and Sourour [3] model was chosen for the degree of cure modeling. This model given by equation (2) is the most common one in the literature for epoxy systems and accounts for an autocatalytic reaction in which the initial reaction rate is not zero.

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

$$K_1 = A_1 \cdot \exp\left(\frac{-E_1}{RT}\right) \text{ and } K_2 = A_2 \cdot \exp\left(\frac{-E_2}{RT}\right)$$

where α is the resin conversion ($0 < \alpha < 1$), T the temperature, R universal gas constant and m, n, A_1, A_2, E_1, E_2 are constants which are calculated from the curve fit using the heat release rate measured by isothermal DSC, K_1 and K_2 are Arrhenius constants dependent on temperature. The constant K_1 was calculated graphically as the initial reaction rate at time zero, given by the intersection of plots of conversion rate versus time.

At the beginning of a curing reaction, the rate of reaction is dominated by the reactivity of the molecule [4]. Cure becomes more and more diffusion controlled as it progresses [4-8]. To

consider this diffusion effect the semi-empirical relationship (Eqn. 3) proposed by Fournier et al. [5] was chosen. Fournier et al. [5] added to the Kamal-Sourour model a diffusion factor $f_d(\alpha)$

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1-\alpha)^n \cdot f_d(\alpha) \quad (3)$$

$$\text{with } f_d(\alpha) = \left[\frac{2}{(1+\exp[(\alpha-\alpha_f)/b])} - 1 \right]$$

where α_f is the conversion at the end of degree of isothermal cure and b is an empirical diffusion constant of the material. The $d\alpha / dt$ versus α experimental curves were fitted with a least-square curve fitting method using the Levenberg-Marquardt algorithm and this procedure gave the values of all kinetic parameters. Parameters n and α_f are evolving linearly with the temperature and parameter m was considered constant and fixed at $m = 0.74$. Table 1 presents Kamal and Sourour corresponding coefficients with diffusion for the LY556 epoxy blend.

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

m	b	A_1 (s^{-1})	A_2 (s^{-1})	E_1 (KJ/mol)	E_2 (KJ/mol)
0.74	0.0452	$1.779e^{+5}$	$1.226e^{+9}$	63.647	85.979

Chemical Shrinkage

Recently, in-situ chemical shrinkage of epoxy resins was examined by Li et al. [9], which established a bilinear relationship for cure shrinkage versus degree of cure, with a break point at gelation. As Li et al. [9] 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 and details are available in [10].

Matrix Thermal Strain Estimation during Cure

Matrix temperature is variable and non uniform during the curing. This heterogeneous temperature field generates thermal 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 coefficient of thermal expansion of the blend.

$$d\varepsilon_{\text{thermal}}^{\text{Vol}}(t) = \alpha_T(t) \Delta T \quad (4)$$

with $\alpha_T(t) = [1 - \alpha(t)] \alpha_{T \text{ liquid epoxy}} + \alpha(t) \alpha_{T \text{ solid epoxy}}(t)$, where $\alpha_{T \text{ liquid epoxy}}$ denotes the thermal expansion coefficient per unit volume of the epoxy resin in its liquid state before gelation and $\alpha_{T \text{ solid epoxy}}$ is the thermal expansion coefficient per unit volume for the fully cured epoxy matrix.

However, for amorphous polymers like epoxy resins, $\alpha_{T \text{ solid epoxy}}$ is temperature and glass transition dependent. Identification of thermal expansion coefficients for the LY556 epoxy system was performed by DMA-TMA analysis. We obtained $\alpha_{T \text{ liquid epoxy}} = 5^{E-4} \text{ } ^\circ\text{C}^{-1}$, $\alpha_{T \text{ solid epoxy}} = 450^{E-6} \text{ } ^\circ\text{C}^{-1}$ for a vitreous matrix (below glass transition temperature T_g) and finally, $\alpha_{T \text{ solid epoxy}} = 450^{E-6} + 4.1^{E-6} (T-T_g)$ for a rubbery matrix (above T_g). This model requires knowledge of T_g at each time during resin cure. The temperature T_g was calculated by the usual Pascault and Williams [11] relation (also called Dibeneditto equation) as follows:

$$\frac{T_g - T_{g0}}{T_{g \text{ infini}} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (5)$$

where λ is an adjustable, structure-dependent parameter ranging between 0.46 and 0.58 for several amine epoxy systems. T_{g0} (T_g at $\alpha = 0$) is the lower limit temperature at the beginning 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, which is physically unachievable. The modulated differential scanning calorimeter (MDSC) measurements were performed with the TA 2920 DSC with the MDSCTM option at a heating rate of 2°C/min with a modulated amplitude of 1°C. A 60s period was allowed to determine the glass transition temperature. The reacting sample used was 8-15 mg. The values measured of T_{g0} and $T_{g \text{ infinity}}$ by first cooling of this partially sample from -50°C and then heated to 200°C were -37°C and 136°C respectively. The value $\lambda = 0.57$ was determined by curve fitting with the experimental data giving the evolution of T_g as a function of temperature.

Specific Heat Cp (J/gK) and Thermal Conductivity λ (W/mK)

The differential scanning calorimeter TA 2920 with the MDSCTM option was used to determine the Cp evolution versus temperature for the uncured resin and the fully cured matrix. The temperature and Cp were calibrated by using indium and sapphire respectively. In the same manner as previously, it was assumed that specific heat evolution during cure can be described by the rule of mixture weighted by the degree of cure between the liquid state (resin) and the solid state (matrix) as follows:

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

where $C_p(0, T)$ and $C_p(1, T)$ stand for liquid resin and fully cured matrix temperature dependant specific heat evolutions. Note that a dependence on T_g was introduced for $C_p(1, T)$. In the same way as for the specific heat, thermal conductivity was expressed by a linear rule of mixture as follows:

$$\lambda(\alpha, T) = (1 - \alpha) \lambda(0, T) + \alpha \lambda(1, T) \quad (7)$$

Heat Flow Associated with 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 mass enthalpy variation ΔH^f of the reaction (Eqn. 8). Thanks to DSC analysis temperature dependency for ΔH^f was taken into account and was found following a linear evolution that ends at an ultimate value of 354 ± 25 J/g.

$$\phi(t) = \rho \Delta H^f(T) d\alpha/dt \quad (8)$$

Mechanical Behavior

Linear elasticity with small strain was considered here. According to DMA shear tests more appropriated for the resin curing analysis, the elastic constitutive law could be written as follow:

$$\sigma(t) = [K(\alpha) - \frac{2}{3} G'(\alpha)] \text{tr}(\varepsilon(t)) \mathbf{I} + 2 G'(\alpha) \varepsilon(t) \quad (9)$$

The elastic shear modulus $G'(\alpha)$ was measured by DMA analysis for a 120°C isothermal curing. The evolution of the bulk modulus as a function of the degree of cure ($K(\alpha)$) was estimated by the rule of mixture between 3 GPa. for the liquid state and 6.3 GPa. for the solid state [12].

FEM Simulation

Finite element analysis was performed with the finite element software Abaqus® V. 6.5.1. From a technical point of view, solving the heat Eqn. (1) coupled with cure kinetics (Eqn. (2)) and the production of heat produced by the thermosetting reaction (Eqn. (8)) were developed with a user material subroutine of Abaqus (UMAT), hence allowing the study of 3D composite structures. The aim of the simulation is to solve the coupling problem on one hand, and on the other hand, perform a parametric study to assess the impact of each coupling on the chemical and thermal strain mechanisms and hence on the development of internal stress. Details on the FEM solver are available in [2].

RESULTS

Local Temperature Simulation

A steel test tube with a diameter of 32 mm filled with epoxy resin for a height of 30 mm was placed in an oven and heated with a 3°C/min ramp followed by an isothermal plateau at 100°C. Four Thermocouple probes were placed inside of the resin for the record of internal temperature evolution. Comparisons between prediction and measurements are displayed in Fig. 1 and are almost satisfying.

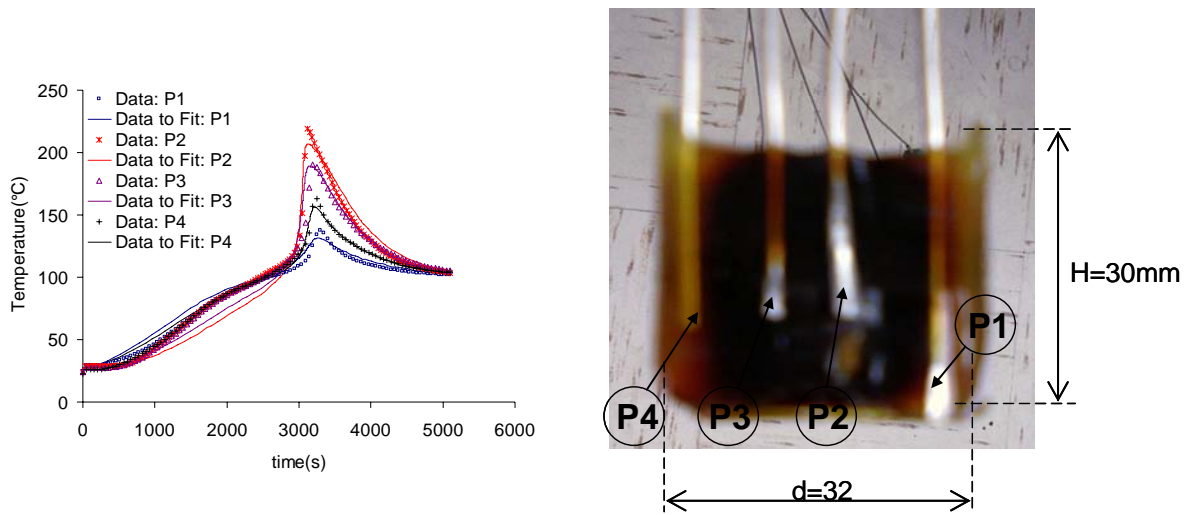


Fig. 1 Thermal gradients measured and predicted during the cure of the LY556 epoxy resin (ramp $3^{\circ}\text{C}/\text{min}$ and 100°C plateau).

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 the next subsection.

Internal Stress Prediction

Cure was carried out 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 $3^{\circ}\text{C}/\text{min}$ 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 exothermic effect was observed with a peak at around 250°C . The elastic constitutive law of the matrix in formation is determined by the local degree of cure information as indicated by Eqn. (9) and elastic analysis of the epoxy Pyrex test tube structure leads to a first estimation of the internal stress field developed during resin cure as exposed in Fig. 2.

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 Fig. 3, the stress level calculated for the Pyrex test tube is much higher than the failure stress for Pyrex. Strong strain and stress gradients are observed inside of the matrix in formation. In particular, stress gradients around 7-8 MPa are obtained after gelation start (from 1000s). This is an important result providing confirmation of considerable internal stress development during resin cure.

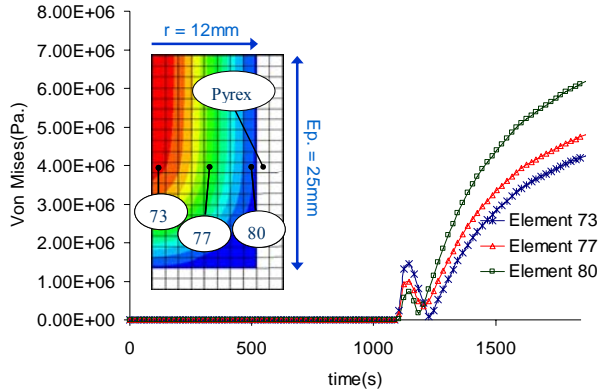


Fig. 2 Von Mises internal stress.

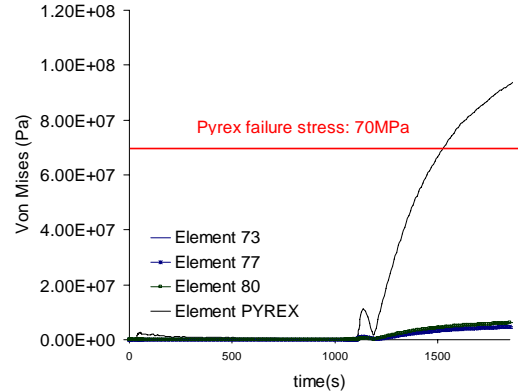


Fig. 3 Von Mises stress for Pyrex test tube.

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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