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# MULTI-SCALE MODELING OF TIME-DEPENDENT THERMAL EXPANSION AND CHEMICAL SHRINKAGE DURING THE CURING PROCESS OF POLYMER MATRIX COMPOSITES

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**Keywords:** viscoelasticity, thermal expansion, chemical shrinkage, injection pressure, residual stress

## Abstract

A multi-scale modeling strategy for the simulation of the stress evolution in a composite material during the curing process is presented. It consists of a coupled thermo-kinetic simulation of the evolution of temperature and degree of cure taking into account heat transfer and the exothermal reaction enthalpy, and a thermo-mechanical simulation taking into account the thermal expansion of the material, the volume loss of the resin due to chemical shrinkage and the resin added during the curing process to maintain the consolidation pressure. The temperature and cure dependent viscoelastic properties and expansion coefficients are obtained from the constituent properties by homogenization. Due to the viscoelastic behavior of the resin, the resulting expansion coefficients are time-dependent. The effect of the resin injection is modeled by an additional parametric strain accounting for the volume change of the resin in the same way as the volume loss due to chemical shrinkage. The added resin quantity is an additional degree of freedom that evolves with the aim of reaching equilibrium between the injection pressure and the pressure in the mold. With increasing resin viscosity, the change of resin quantity is slowed down, leading to a pressure drop when the resin passes the gel point.

## 1. Introduction

The generation of residual stresses in polymer matrix composites is a complex multi-physics and multi-scale process. The polymerization kinetics of the resin during the curing process can, in general, phenomenologically well be described by an autocatalytic model [1] for the evolution of the degree of cure, which depends on temperature and the current state of cure. The polymerization reaction is exothermal, thus influencing the temperature evolution in the composite part. Residual stresses are generated due to a volume loss of the resin during the polymerization (chemical shrinkage) and the different coefficients of thermal expansion (CTE) of the fibers and the matrix. The amount of residual stresses and their impact on the part shape and damage onset and evolution is influenced by the mechanical behavior of the constituent materials, which in the case of the resin strongly depends on temperature and degree of cure [2]-[4]. Residual stresses are present at each characteristic scale of the composite, starting from the micro-scale due to the mismatch between the expansion coefficients of the fibers and the matrix, over the meso-scale where the architecture of the fibrous reinforcement is defined, up to the macro-scale of the structure where residual stresses have an impact on the final shape of the composite part.

Numerical simulation of the generation of residual stresses thus requires constitutive models that take into account the different physics involved and appropriate scale change methods. In this contribution,

we present a multi-scale modeling strategy that consists of a thermo-kinetic simulation of the evolution of temperature and degree of cure and a thermo-mechanical simulation of the evolution of the internal stresses. The thermo-kinetic simulation takes into account the exothermal reaction enthalpy of the polymerization and the heat transfer within the composite and between the composite and the mold. The evolutions of temperature and cure in time at each integration point are taken as locally varying input parameters to the thermo-mechanical simulation. They drive the chemical shrinkage and the thermal expansion and influence the mechanical behavior of the material. The influence of the resin injection pressure is modeled phenomenologically by means of an additional parametric strain that accounts for the increase of the resin volume in the composite during the curing cycle, which compensates partially the volume loss due to chemical shrinkage. If the consolidation pressure decreases significantly before the degree of cure of the resin reaches a critical value, gas bubbles may nucleate leading to porosity in the composite part [5]-[6]. With the proposed approach, the pressure drop caused by the chemical shrinkage of the resin can be estimated and the risk of porosity formation can be evaluated.

For the mechanical behavior of the composite, a viscoelastic constitutive behavior with time-dependent expansion coefficients is used [8], which is obtained by homogenization [7]-[8] from the behavior of its constituents [4]. The formulation of the model and the homogenization method are briefly described in section 2. In section 3, the thermo-kinetic simulation of the curing process is presented. The thermo-mechanical simulation with the approach to take into account the influence of the resin injection pressure is described in section 4. Some results of the stress evolution in a composite plate obtained with the presented modeling strategy are shown in section 5.

## 2. Viscoelastic homogenization with time-dependent expansion coefficients

### 2.1. Viscoelastic behavior

The viscoelastic behavior of the resin and the composite is modeled by a 3D anisotropic version of a generalized Maxwell model [7]. The stress evolution is given by

$$\underline{\sigma}(\xi) = \left( \underline{E}_\infty + \sum_{k=1}^N \underline{E}_k \right) : \underline{\varepsilon}^{ve}(\xi) - \sum_{k=1}^N \underline{E}_k : \underline{\varepsilon}_k^{ve}(\xi) \quad (1)$$

where  $\underline{E}_\infty$  is the asymptotic relaxed stiffness tensor of the material and  $\underline{E}_k$  are the coefficients of the Prony series expansion of the relaxation master curves.  $\underline{\varepsilon}^{ve}$  is the viscoelastic part of strain (see section 2.2) and  $\underline{\varepsilon}_k^{ve}$  are internal variables accounting for the strain history. Their evolution is given by

$$\frac{d\underline{\varepsilon}_k^{ve}(\xi)}{d\xi} = \frac{1}{\tau_k} (\underline{\varepsilon}^{ve}(\xi) - \underline{\varepsilon}_k^{ve}(\xi)) \quad (2)$$

$\xi$  is a reduced time that describes the horizontal shifts of the relaxation curves along the logarithmic time scale upon change of temperature and degree of cure under the assumption of time-cure-temperature superposition [9]:

$$\xi(t) = \int_{-\infty}^t \frac{1}{a_T(t')} dt' \quad (3)$$

For the polymer matrix, the tensors  $\underline{E}_k$  and  $\underline{E}_\infty$  take an isotropic form. Creep is supposed to be isovolumetric, hence the  $\underline{E}_k$  are purely deviatoric. The experimentally observed shear relaxation master

curves are well reproduced by Prony series whose coefficients follow a continuous function of the form [4]

$$G(\tau) = A \exp\left(-\left(\frac{\log_{10} \tau - \log_{10} \tau_{peak}}{l_{peak}}\right)^2\right) + \frac{B}{2} \left(1 - \operatorname{erf}\left(\frac{\log_{10} \tau - \log_{10} \tau_{peak}}{l_{peak}}\right)\right) \quad (4)$$

Taking one relaxation time per decade provides a sufficiently smooth relaxation curve in good agreement with the experimental data [4]. For the viscoelastic behavior of the consolidated tows at the meso-scale and for the average behavior of the composite over a representative volume element (RVE), the tensors  $\underline{E}_k$  and  $\underline{E}_\infty$  are anisotropic and obtained from the homogenization procedure described in section 2.3. Besides the anisotropy of these tensors, the formulation of the model is the same.

## 2.2. Time-dependent expansion coefficients

In a small-strain framework, we use an additive decomposition of the strain tensor into a mechanical (viscoelastic) part  $\underline{\varepsilon}^{ve}$  that is used in the constitutive behavior presented before, a thermal part  $\underline{\varepsilon}^{th}$  that is caused by a temperature change, and a chemical part  $\underline{\varepsilon}^{ch}$  that is caused by the volume loss of the resin during polymerization.

$$\underline{\varepsilon} = \underline{\varepsilon}^{ve} + \underline{\varepsilon}^{th} + \underline{\varepsilon}^{ch} \quad (5)$$

The mismatch in the CTE between the fibers and the matrix causes internal stresses in the composite if the temperature changes. Due to viscoelastic phenomena, such as creep and relaxation, these stresses evolve in time after a temperature change even if the temperature is kept constant. As a result, the average strain of the composite also evolves in time after a temperature change. This effect is modeled following a formulation proposed in [10] with a time-dependent CTE, which if written in terms of a Prony series, leads to a formulation similar to the generalized Maxwell model described in the previous section. The evolution of the thermal strain as a function of the reduced time (Eq. 3) is then given by [8]

$$\frac{d\underline{\varepsilon}^{th}(\xi)}{d\xi} = \left( \underline{\alpha}_\infty^{th}(T(\xi), c(\xi)) - \sum_{k=1}^N \underline{\alpha}_k^{th}(T(\xi), c(\xi)) \right) \frac{dT(\xi)}{d\xi} - \sum_{k=1}^N \frac{1}{\tau_k} \underline{\varepsilon}_k^{th}(\xi) \quad (6)$$

with internal variables  $\underline{\varepsilon}_k^{th}$  accounting for the history of temperature and the CTE. Their evolution is given by

$$\frac{d\underline{\varepsilon}_k^{th}(\xi)}{d\xi} = \underline{\alpha}_k^{th}(T(\xi), c(\xi)) \frac{dT(\xi)}{d\xi} - \frac{1}{\tau_k} \underline{\varepsilon}_k^{th}(\xi) \quad (7)$$

The tensorial coefficients  $\underline{\alpha}_\infty^{th}$  and  $\underline{\alpha}_k^{th}$  of the Prony series expansion may depend on temperature and degree of cure, hence the slightly different formulation compared to the viscoelastic model presented in section 2.1. An exactly equivalent formulation can be used for the coefficients of chemical shrinkage (CCS), setting the CCS of the fibers to zero.

## 2.3. Homogenization

As shown in various works ([11] cited here only as an example), the generalized Maxwell model is obtained from the integral form of viscoelasticity if the time-dependent relaxation function is written in

terms of a Prony series. If the Laplace-Carson (LC) transform is applied to the integral form of a linear viscoelastic behavior, a relation equivalent to a linear elastic behavior is obtained, with a stiffness tensor that depends on the LC transform parameter. This well-known formalism was extended in [8] to time-dependent CTE written in the formulation of [10], leading to a thermo-elastic relation in the LC space. If Prony series are used for the relaxation function and the time-dependent CTE, the LC-transform can be written by a system of equations [7] for the relaxation function

$$\hat{\underline{E}}(p_i) = \underline{E}_\infty + \sum_{k=1}^N \mathcal{L}_{ik} \underline{E}_k \quad (8)$$

where  $\hat{\underline{E}}(p_i)$  is the LC transform of the relaxation function evaluated at a LC-transform parameter  $p_i$  and  $\mathcal{L}_{ik}$  are given by

$$\mathcal{L}_{ik} = \frac{p_i}{p_i + \frac{1}{\tau_k}} \quad (9)$$

The LC transform of the time-dependent CTE for a given temperature  $T$  and degree of cure  $c$  is given by

$$\hat{\underline{\alpha}}^{th}(p_i, T, c) = \underline{\alpha}_\infty^{th}(T, c) - \sum_{k=1}^N \mathcal{L}_{ik} \underline{\alpha}_k^{th}(T, c) \quad (10)$$

The same formulation is used for the CCS.

The LC transform of the relaxation function and the time-dependent expansion coefficients is then obtained with classical thermo-elastic homogenization methods. If we assume that the relaxation function and the expansion coefficients of the homogenized material can also be well fitted by a Prony series with weights that follow continuous functions if plotted against the logarithm of the relaxation times, we can choose the same relaxation times as for the matrix behavior to discretize these continuous spectra. Then, if we determine the LC transform of the homogenized behavior for at least  $M \geq N$  different  $p_i$ , the homogenized behavior in the time-domain is obtained by solving the least squares problems given in Eqs. (8) and (10) to obtain the coefficients  $\underline{E}_k$  and  $\underline{\alpha}_k^{th}$  of the homogenized material. Since this problem is often ill-conditioned, the proper choice of the  $p_i$  is important [7] and sometimes a Tikhonov regularization may be necessary [8]. In the case of a composite with a woven reinforcement, two homogenization steps are needed: the first one to determine the homogenized behavior of the consolidated tows from the constituent (fiber and matrix) behaviors, and the second one to determine the homogenized behavior of the composite.

### 3. Thermo-kinetic simulation of the curing process

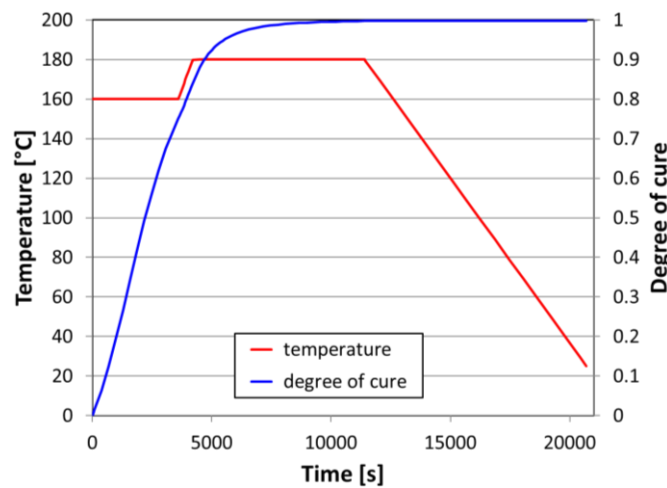
The curing process of a flat plate of composite with a 3D woven reinforcement as the one used in [7]-[8] is simulated. The dimensions of the plate and the curing cycle correspond to those used in [13]-[14]. In the first step of the curing process simulation, the heat transfer equation is solved using the Finite Element (EF) software Z-set [12]. The heat generated by the exothermal polymerization reactions is taken into account by a heat source term that is added to the heat transfer equation:

$$\vec{\nabla} \cdot (\underline{\kappa} \cdot \vec{\nabla} T) = -\rho C_p \dot{T} + \rho H_R \dot{c} \quad (10)$$

where  $\underline{\kappa}$  is the anisotropic 2<sup>nd</sup> order tensor of thermal conductivity of the composite,  $\rho$  is its mass density,  $C_p$  the heat capacity per unit mass and  $H_R$  the reaction enthalpy per unit mass. The evolution of the degree of cure  $c$  is simulated using the autocatalytic model proposed in [1]

$$\dot{c} = (k_1(T) + k_2(T)c^m)(1 - c)^n \quad (10)$$

with reaction velocity coefficients  $k_{1,2}$  that follow a classical Arrhenius dependence on temperature. The heat source term accounts for the overheating that may occur in thick composite parts. However, as the simulated plate is relatively thin (6.7mm), the temperature remains quite homogeneous during the curing process (not more than 0.5°C between the surfaces and the center of the plates). Therefore, the curing temperature is applied directly to the surfaces of the plate. Heat transfer boundary conditions can alternatively be applied, but this does not influence the result if the overheating due to the exothermal reaction is insignificant. The evolution of temperature and degree of cure are shown in Figure 1.



**Figure 1.** Evolution of temperature and degree of cure during the simulated curing cycle.

## 4. Thermo-mechanical simulation of the curing process

### 4.1. Boundary conditions and input parameters

Temperature and degree of cure obtained with the thermo-kinetic simulation are taken as input parameters to the thermo-mechanical simulation. They drive thermal expansion and chemical shrinkage and influence the viscoelastic behavior as described in section 2. The same FE mesh is used as in the thermo-kinetic simulation, so the data is directly transferred at each integration point. The presence of the mold is simulated by a frictionless contact at the top and bottom surface that allows the plate to contract through the thickness but not to expand with respect to its initial state. On the lateral surfaces of the plate, no contact conditions are applied, as there is a small space between the composite and the mold frame. During the curing process, this space is filled with resin at the injection pressure. Therefore, this pressure is applied to the sides of the plate.

### 4.2. Modeling the influence of the resin injection pressure

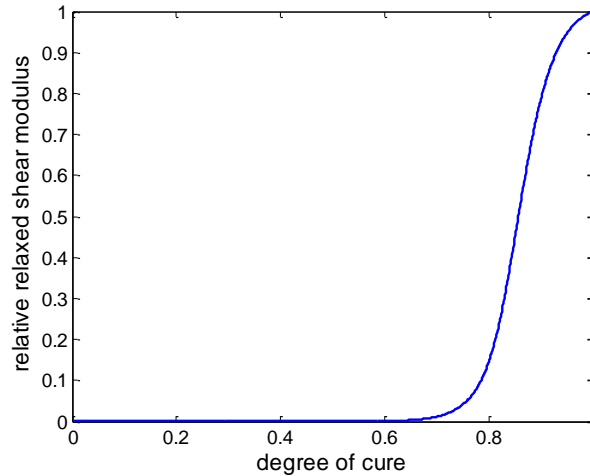
During the curing phase, the resin injection continues at a high pressure in order to compensate a part of the volume loss due to chemical shrinkage and maintain the consolidation pressure in the mold to ensure desorption of gas bubbles until the resin is sufficiently polymerized. The effect of this ongoing injection is modeled in the same way as the chemical shrinkage, as it leads to an increase of the resin

volume in the composite, while chemical shrinkage leads to a volume loss. An additional strain  $\underline{\varepsilon}^{pr}$  is therefore added to Eq. (5) accounting for this volume increase. It follows the evolution given in Eq. (6) and (7) but is driven by the injected resin quantity instead of temperature for  $\underline{\varepsilon}^{th}$  or degree of cure for  $\underline{\varepsilon}^{ch}$ . The expansion coefficient that translates its effect on the composite level is obtained by homogenization in the same way as the CCS of the composite, taking zero expansion for the fibers and the relative volume change for the resin.

The injected resin quantity is unknown and driven by the injection pressure. Therefore, this quantity is added as an additional degree of freedom to the FE problem. The associated residual for the global Newton-Raphson algorithm is the difference between the internal pressure in the mold (the volume average of the trace of the stress tensor) and the applied injection pressure. If the resin is liquid with negligible viscosity, it can flow everywhere in the composite and the equilibrium between pressure in the mold and injection pressure is reached immediately. However, the viscosity of the resin increases with degree of cure, which after the gel point becomes a viscoelastic solid. This transition is taken into account in the viscoelastic model by a Maxwell element with a relaxation  $\tau_{gel}$  that increases exponentially with the degree of cure:

$$\tau_{gel} = t_{load} \exp(a + bc) \quad (10)$$

This leads to an apparent relaxed shear modulus that increases with the degree of cure as shown in Figure 2. This evolution is close to the one observed experimentally by [2] on a different epoxy resin.  $t_{load}$  corresponds to the loading time at which the apparent relaxed shear modulus is measured.



**Figure 2.** Evolution of the ratio between the relaxed shear modulus as a function of cure and its value for the fully cured resin.

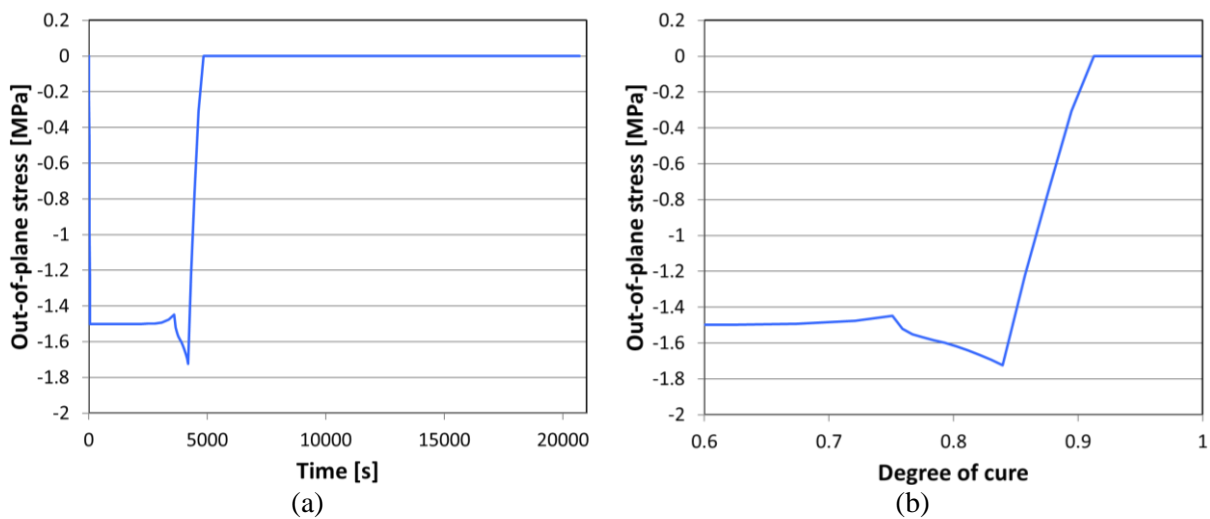
The influence of the resin viscosity on the injection pressure transmission is taken into account by a residual that ensures that relative volume change of the resin in the mold is given by

$$\frac{\dot{V}}{V} = \frac{1}{\eta} (p^{ext} - p^{int}) \quad (10)$$

where  $\eta$  is the viscosity of the resin,  $p^{ext}$  the applied resin injection pressure and  $p^{int}$  the pressure in the mold. The resin viscosity is taken from the viscoelastic model, using for each Maxwell element the product of its shear modulus with the temperature and cure dependent relaxation time.

## 5. Results

The evolution of the out-of-plane stress in the composite plate throughout the curing process obtained with the presented simulation strategy is shown in Figure 3a. In Figure 3b, the out-of-plane stress is plotted against the degree of cure. Comparison with the temperature cycle presented in Figure 1 shows that during the first dwell at 160°C when the resin viscosity is still very low, the out-of-plane stress corresponds to the imposed injection pressure. Towards the end of the 160°C dwell, when the degree of cure exceeds about 60%, the relaxed stiffness of the resin starts to increase (see Figure 2) and thus the chemical shrinkage is no longer immediately compensated. This leads to a small decrease in pressure towards the end of the first dwell (between 60% and 70% of cure, see Figure 3b). During the heating phase up to 180°C, the out-of-plane stress increases due to the thermal expansion of the resin. When the 2<sup>nd</sup> dwell temperature is reached, the pressure starts to decrease immediately, as at this point the resin viscosity is already significant (about 84%, see Figure 3b), and the chemical shrinkage can no longer be compensated by the resin injection. With the present model for the resin viscosity, the out-of-plane stress drops to zero at a degree of cure of about 91%.



**Figure 3.** Evolution of the out of plane stress during the curing process of a composite plate as a function of time (a) and plotted against the degree of cure (b).

## 6. Conclusions

The presented multi-scale modeling strategy takes into account the couplings between the different physical phenomena involved in the generation of residual stresses in polymer matrix composites. With the presented homogenization strategies, the temperature- and cure-dependent material properties can be determined from the constituent behaviors. Due to the viscoelastic nature of the matrix, time-dependent expansion coefficients have to be used for the homogenized behavior of the composite. The ongoing resin injection during the curing phase that compensates part of the chemical shrinkage in order to avoid an early pressure drop is modeled by an expansion coefficient in the same way as the volume loss due to chemical shrinkage, but with an opposite sign. In the present model, this method supposes that the injected resin is distributed homogeneously through the whole composite. Especially in bigger parts, this assumption is in general not true. In these cases, the resin flow during injection has to be modeled beforehand, taking into account the increasing viscosity during the curing process and the permeability of the fibrous reinforcement. The resulting distribution of resin in the reinforcement can be used as heterogeneous input parameter with the presented model in the same way as the temperature and degree of cure obtained with the thermo-kinetic simulation are used for the thermal expansion and the chemical shrinkage in the thermo-mechanical simulation.

The presented test case of a thin flat plate is very simple and avoids most of the heterogeneities. Future work will consist in application of the presented modeling chain to more complex structures, with heterogeneous temperatures (either due to an inhomogeneous heating or overheating caused by the exothermal polymerization), heterogeneous material properties (various reinforcement architectures in one part) and more realistic boundary conditions. In particular, the thermal and mechanical deformation of the mold and the friction and adhesion between part and mold must be taken into account. Furthermore, the small space between the reinforcement and the mold frame is filled with resin and thus more realistically modeled by a thin resin layer around the composite. If these different aspects are correctly taken into account, the proposed modeling chain is able to predict both the evolution of the pressure in the composite during the curing process and the generation of residual stresses and their impact on the final part shape.

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