

Experimental Study of the Induced Residual Stresses During the Manufacturing Process of an Aeronautic Composite Material

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Abstract: A methodology is proposed for predicting the formation and the development of the manufacturing residual stresses, this approach is based on the study of the evolution of the resin yield stress. In order to evaluate our method, a comparison has been made between the yield time (corresponding to the formation of a yield stress) and the gel time. A self-consistent model is used to determine the cure-dependent chemical shrinkage coefficient of the composite material. This model allows considering for the composite material behavior an anisotropic chemical shrinkage, which is not represented by a classical linear model. An experimental approach based on the peel-ply method is used to determine the distribution of the residual stresses through the thickness.

Key words: Epoxy resin composites, manufacturing process, peel-ply method, residual stresses, thermal and mechanical characterizations

INTRODUCTION

The temperature and degree of cure gradients, the chemical shrinkage, the variations of the matrix properties during the curing process and the anisotropy of composites material lead to the development of residual stresses in the manufactured part. In this work, the presence of residual stresses in laminates is emphasized. An experimental approach based on the peel-ply-method is used (Abou-Msalleh, 2008). In this method, the curvatures and moments resulting from the removal of thin plies are measured. This information allows us to retrieve the corresponding stresses. In addition, successive ply removals allow us to deduce a distribution through the thickness of the mechanical fields (Gigliotti *et al.*, 2006; Treuting and Read, 1951). The through-the-thickness measured curvatures (Fig. 1a), and moments (Fig. 1b) show us the presence of the residual stresses and the variations of the mechanical states after peel ply.

In most studies, the residual stresses are determined by considering the temperature difference between the cure and ambient temperatures assuming that no stress occurs before cool-down (Hahn, 1976; Griffin, 1983). So, the modeling has to be improved to take into account the variations of the properties with cure and a better representation of the effective composite properties is needed to well determine the residual stresses formation before cool-down.

A key factor contributing to the residual stresses development is the chemical shrinkage of the resin during

the cross-linking polymerization reaction. Many authors have emphasized the importance of the volumetric shrinkage and studied the influence of this phenomenon on the curing stress development for thick composite pieces (White and Kim, 1998; Ruiz and Trochu, 2005). In these preceding studies, the chemical shrinkage is taken as isotropic.

Another important point is the onset of the residual stress formation during cure. Generally, the gel point of the resin is considered as a criterion for the appearance of residual stresses. However, its definition is still very blurred in the mechanical sense.

It is interesting to approach this characteristic of polymers by considering that the stresses begin to form when the resin has a yield stress. During the manufacturing process, the resin passes from a liquid, without yield stress, to a solid state with a corresponding yield: in this case, the residual stresses can remain in the composite parts if they are below than the yield stress of the resin, if they exceed this yield stress, a relaxation is possible.

The aim of the present work is to study the influence of the anisotropic chemical shrinkage and resin yield stress on the residual stresses development in thermosetting composites. A one-dimensional thermo-chemo-mechanical model is used to predict the distribution of the through-the-thickness temperature, degree of cure and residual stresses

A self-consistent model is employed to determine the instantaneous spatially varying mechanical properties,

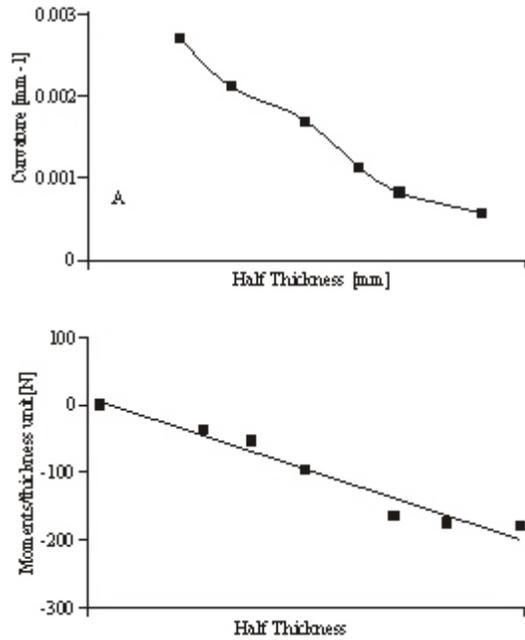


Fig. 1: Measured curvatures (a) and moments (b) after peel ply removal in asymmetric laminates

thermal expansion and chemical shrinkage within the composite materials and that by considering the resin and fibers constituent behaviors. This approach allows taking into account an anisotropic chemical. The characterization of the resin yield stresses during cure is performed; these stresses could be taken as a criterion for the relaxation of residual stresses during the process.

MATERIALS AND METHODS

Effective chemical shrinkage: The composite properties are highly dependent on the fiber and resin properties, and of the fiber volume fraction. A self-constituent model is used to compute the mechanical properties, the coefficients of thermal expansion and chemical shrinkage from the properties of the constituents. This approach permits to take into account an anisotropic chemical shrinkage for the composite material; this is not the case with classical linear models.

Self-consistent model: The self-consistent model, based on the formalism developed by Eshelby (1957) and Kröner (1958), allows estimating the effective behavior of composite materials.

In our model, the fibers are treated as ellipsoidal inclusions embedded in an infinite environment, called equivalent homogeneous medium (Jacquemin *et al.*, 2004). The properties of the equivalent medium are performed by homogenization operations from the properties of the matrix and fiber constituents. If

the elementary inclusions (here the matrix and the fiber) have ellipsoidal shapes, stresses and strains are connected by the following relation of scale transition:

$$\overline{\overline{\sigma}} - \overline{\sigma} = -\overline{\overline{C}} : \overline{R} : (\overline{\overline{\epsilon}} - \overline{\epsilon}) \quad (1)$$

Where, $\overline{\overline{\sigma}}$ and $\overline{\sigma}$ are respectively the stress tensors of the constituents at microscopic and macroscopic scales, $\overline{\overline{\epsilon}}$ and $\overline{\epsilon}$ are the strain tensors, $\overline{\overline{C}}$ is the homogenized stiffness tensor and \overline{R} is the reaction tensor depending on global behavior through the following expression:

$$\overline{R} = \left(\overline{\overline{C}^{-1}} - \overline{E} \right) : \overline{E}^{-1} \quad (2)$$

\overline{E} , the Morris tensor, expresses the dependence of the reaction tensor to the morphology of the constituents. Macroscopic stresses and strains are equal to the average of constituent stresses and strains (Winter, 1987):

$$\langle \overline{\overline{\sigma}} \rangle_{r-f.m} = \overline{\sigma} \quad (3)$$

$$\langle \overline{\overline{\epsilon}} \rangle_{r-f.m} = \overline{\epsilon} \quad (4)$$

The self-consistent model allows determining the effective tensors of stiffness, thermal expansion and chemical shrinkage of the composite ply from the mechanical, thermal and chemical properties of the constituents (Abou-Msalleh, 2008) and that by using the preceding equations. The variations of the chemical shrinkage coefficients during cure for a unidirectional reinforced composite are depicted on Fig. 2. An anisotropic chemical behavior is considered: the shrinkage in the longitudinal direction (CCS_1) is near to zero, this direction is governed by the fiber and this is not the case in the transverse direction (CCS_2) where the resin behavior is predominant. This result has a great influence on the estimation of curing residual stresses due to the chemical shrinkage.

Resin yield stress: In this part, the evolution of the resin yield stress during cure is studied. Epoxy resin is a reactive system and its state changes during the reaction. It passes from a viscous liquid condition, which "flows"

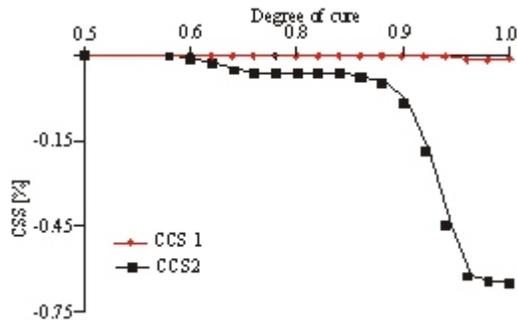


Fig. 2: Coefficients of chemical shrinkage vs degree of cure (unidirectional composites)

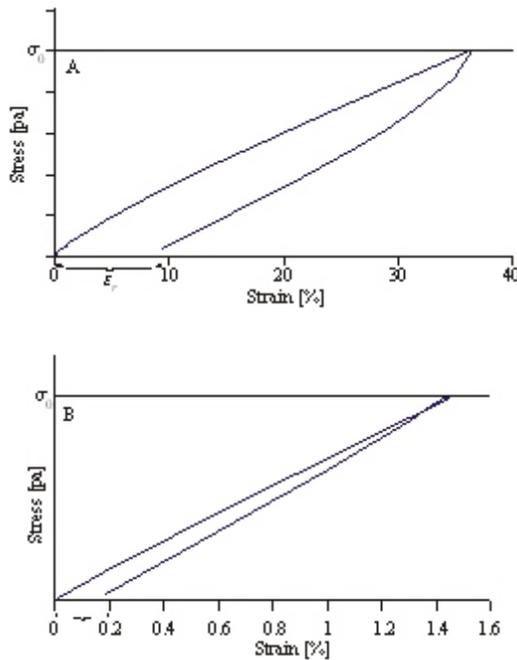


Fig. 3: Measured stress as a function of strain, (a) non-elastic behavior, (b) elastic behavior

under weak stresses, to a solid state which has a yield stress. If the residual stresses exceed this yield stress, they relax; but if they are lower than the yield stress, they remain in the composite part. The main originality in this approach is the use of a rheometer, which is usually used in the determination of stress-strain rate curve, to obtain the yield stress.

Experimental characterization: A rheometer is not a suitable tool to check if a material has an elastic behaviour. Indeed, this type of equipment is used to study the viscous and viscoelastic materials, it measures traditionally the stress response as a function of strain rate. In what follows, we propose an original method for

using an imposed-stress rheometer similar to a tension machine. We used the “creep” mode of the rheometer and that for imposing to the resin a stress cycle. The chosen form is a linear rise followed by a discharge with a rate, slow enough so that the stress is properly established, but fast enough that the material does not change, with curing, during the test. Measuring the angle of rotation of the rheometer plate allows, from an inverse calculation, getting the strain. So, the stress-strain curve is plotted and the residual strain (ϵ_r) is analyzed. We can say that the stress has always been less than the yield stress, if the residual deformation (ϵ_r), after return to a null stress, is less than a limit called “offset”, which is fixed in what follows at 0.2%.

Our method is as follows: 1. The samples are cured at a given isotherm. At a time t corresponding to a known temperature, a cycle charge / discharge (with an imposed stress σ_0) is applied. If the response in strain shows a non-elastic back (Fig. 3a), it means that the imposed stress σ_0 exceeds the yield stress of the resin. So, we repeat our experience later until that an elastic return is obtained (offset = 0.2%) (Fig. 3b). Get an elastic return means that the imposed stress σ_0 is just below the yield stress of the resin and thus the time corresponding to this stress is determined. This time is used to deduce the degree of cure corresponding to this yield stress at a given temperature. The variation of the degree of cure with time at different temperatures is given by the kinetic model (Bailleul *et al.*, 1996):

$$\frac{d\alpha}{dt} = F(T) \cdot G(\alpha) \quad (5)$$

where, α is the degree of cure, and T is the temperature. 2. Tests are carried out at different isotherms. The time of the test must be sufficiently small to make the assumption that the degree of cure remains constant (which is not easy for high temperatures). In addition, we must be careful to not damage our material and be careful in the choice of the applied stress depending on the state of our material. Another problem is the weak rheometer capacities that implies for measuring high yield stresses to employ a tensile test machine (Abou-Msallem, 2008).

RESULTS AND DISCUSSION

Fig. 4a shows the evolution of yield stress according to the degree of cure for a temperature of 160°C. We can see in this figure the degree of cure corresponding to the formation of the yield stress (α_{yield}). The time corresponding to the formation of a yield stress (t_{yield}), varies with temperature (Fig. 4b).

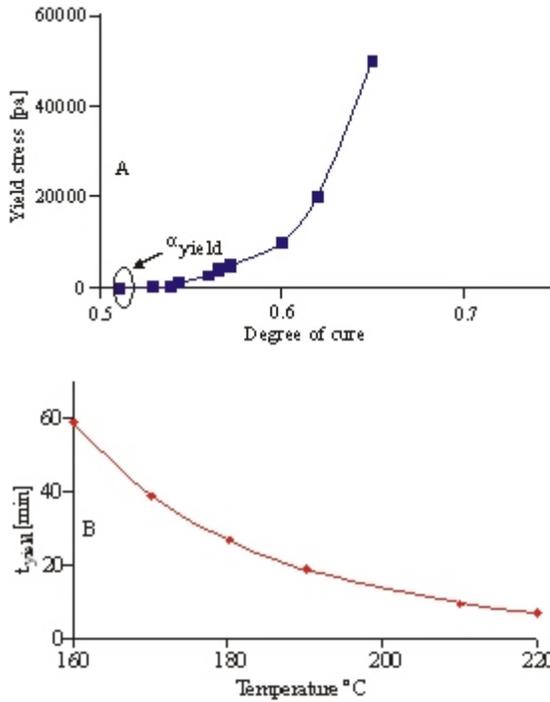


Fig. 4: (a) Yield Stress as a Function of Degree of Cure, (b) Yield Time as a Function of Temperature

By analyzing Fig. 4, we can note that:

- The resin yield stress increases with time and degree of cure, because the resin becomes increasingly rigid and passes from a viscous liquid state to a rigid solid state.
- The variation of the yield time (t_{yield}), as a function of temperature, is obtained.

The degree of cure at t_{yield} (α_{yield}) is determined by considering the kinetic model (Eq. 5). Since, isothermals are considered, α_{yield} is deduced by integrating $G(\alpha)$ between 0 and t_{yield} . We get $\alpha_{yield} = 0.52 \pm 0.01$ for all considered isotherms. A crucial point is that the yield point of our resin is temperature independent.

In order to evaluate our method, a comparison has been made between t_{yield} and the gel time (t_{gel}). A dynamic mechanical measurements are used to determine this gel point;

Rheological characterization: For the characterization of the gel point, dynamic rheological measurements are performed, with an ARG2, parallel plates imposed-stress, Rheometer (the same used in the characterization of the yield stress). We prepare a 550 mg resin sample which represents a sufficient quantity for the gap (0.8 mm) between the rheometer parallel plates (25 mm of diameter). Tests are carried out at different isotherms (between 160°C and 210°C). At each isotherm, frequency

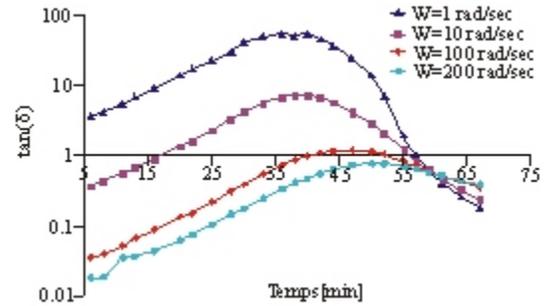


Fig. 5: Loss factor $\tan(\delta)$ as a function of time at different frequencies at 160

Table 1: Gel time at different isotherms

| Temperatures (°C) | 160 | 170 | 180 | 190 | 200 | 210 |
|-------------------|-----|-----|-----|-----|-----|-----|
| Gel time (min) | 52 | 34 | 24 | 14 | 9 | 6 |

scans are performed at different times during the resin curing. Four frequencies are chosen: 1, 10, 100 and 200 rd/s. This frequencies range allows us to scan more or less rapid. The time of the scanning test must be sufficiently small to make the assumption that the conversion degree remains constant during testing (which is not easy for high temperatures). In addition, we must be careful to not damage our material and be careful in the choice of the applied stress depending on the state of our material (low stress at the beginning of the test and a high stress at the end when the resin becomes more rigid).

In general for determining this gel time, we can use different methods: the first one is based on the intersection of $G' - G''$ (elastic and viscous shear modulus). This method is not so good because the gel time vary with frequencies (Winter, 1987). The two other methods are based on the intersection of $\tan \delta$ (loss factor is given by

$$\tan \delta = \frac{G'}{G''}$$

and viscosity divergence.

By plotting the loss factor as a function of time for different frequencies (Fig. 5), the gel time is determined at the intersection of $\tan(\delta)$ curves (Winter, 1987), where;

$$\tan(\delta) = \frac{G''(\omega)}{G'(\omega)}$$

with $G'(\omega)$ and $G''(\omega)$ are respectively the elastic shear modulus and the viscous shear modulus. At the intersection, $\tan(\delta)$ is equal to 0.6 ± 0.01 (1). It means that viscous modulus and elastic modulus are not equal at this point. Table 1 presents the results obtained for the gel time at different isotherms.

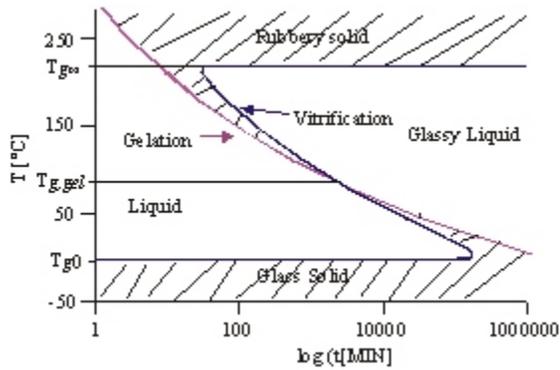


Fig. 6: TTT diagram

We can now determine the gel point (α_{gel}), the degree of cure corresponding to the gel time, by using our kinetic model (Eq. (5)) and the results for t_{gel} (Table 1). The gel point is determined by integrating $F(T).G(\alpha)$ between 0 and t_{gel} .

It is found that this gel point is temperature independent ($a_{gel} = 0.52 \pm 0.01$), which is the same as α_{yield} .

Also by knowing the gel times of the resin (Table 1) we can plot the gelation curve (Fig. 6) (temperatures as function of gel times). An exponential form is presented. In fact, this is due to the exponential variation of the polymerisation rate with temperature. This gelation curve is determined theoretically by integrating the inverse of the polymerisation rate (Eq. (5)) between 0 and α_{gel} .

The knowledge of the change in glass transition temperature with the conversion T_g is modeled by the relation of Pascault *et al.* (2002), (Eq. (6)):

$$T_g(\alpha) = T_{g0} + \frac{(T_{g\infty} - T_{g0}) \lambda \alpha}{[1 - (1 - \lambda) \alpha]} \quad (6)$$

$T_{g\infty}$ and T_{g0} are the glass transition temperature for the cured and uncured resins respectively, λ is a material constant which is determined by using an iterative process based on the least squares method. The variation of the degree of cure with time, allow drawing the vitrification curve (Fig. 6). The vitrification time (t_{vit}) corresponding to a given glass transition temperature is determined by integrating the inverse of the polymerization rate between 0 and $\alpha(T_g)$.

By plotting the gelation and vitrification curve, we determine the TTT diagram (Time-Temperature - Transformation) which characterizes the material states (Fig. 6).

This method is good and the results are coherent with those obtained by our method for t_{yield} ($t_{gel} \approx t_{yield}$). This means that the idea of taking the gel point as a criterion

for the appearance of residual stresses is not false but consider α_{yield} presents a mechanical sense. In addition, with our method, we can determine also the yield stress which will be used as a criterion for the residual stresses relaxation. For example, if the residual stresses during cure are more important than the resin yield stress, we will have a stress relaxation without the use of viscoelasticity.

In the next section, we will calculate the residual stresses during curing and the influence of the resin yield stress and anisotropic chemical shrinkage on these residual stresses will be discussed.

Application to cure: The residual stresses calculation during the manufacturing process of composite materials is based on the knowledge of the mechanical states (strain ϵ , stress σ), thermal (temperature T) and kinetic of reaction (degree of cure α) histories.

The determination of residual stresses is carried out in two stages. The first stage is to consider the coupled thermo-kinetic problem due to the manufacturing process. The resolution of the heat equation allows determining the temperature, and the progress of the polymerization reaction is deduced by integrating the kinetic law (Abou-Msallem *et al.*, 2008). The second stage consists, from the constitutive behavior law, to calculate the induced residual stresses from the thermal and chemical strains.

The conduction heat transfer is assumed unidirectional. The equation of heat transfer is used, without thermo-mechanical coupling, with a source term representing the reaction kinetic. The properties of the fibers are assumed constants. The properties of the resin vary with temperature and degree of cure. The variation of the specific heat with temperature and degree of cure is determined by using a Differential Scanning Calorimetry (DSC) technique. The thermal conductivity of the resin and his variation with temperature and degree of cure is characterized by using an instrumented specific mould (Abou-Msallem *et al.*, 2008).

Regarding the boundary conditions of the thermal problem, the curing temperature is imposed on top and bottom surfaces of the plate and a thermal insulation is considered for the side faces.

Once the thermo-kinetic problem solved, the strains corresponding to the thermal expansion and chemical shrinkage induce residual stresses at the macroscopic ply scale and at the local scale. The local residual stresses are compared to the resin yield stresses to know if a stress relaxation takes place.

Resin yield stress: In order to know if the process induced residual stress exceeds, at a given time, the resin yield stress, the case of a pure resin plate with 5 mm thickness is considered. The curing cycle used in this

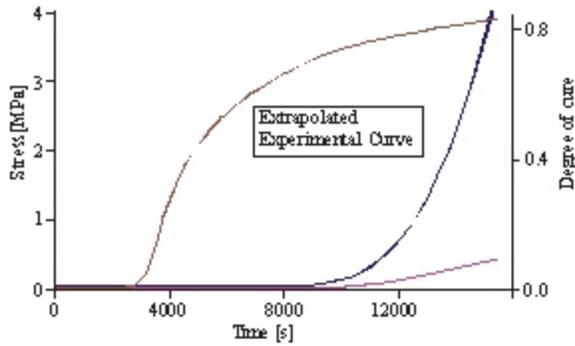


Fig. 7: Comparison between resin yield stress and calculated residual stress

example is composed of a heating ramp from 20 to 160°C and a plateau at 160°C during 180 mn. After the one dimensional simulations of the temperature and degree of cure, the time corresponding to α_{yield} is determined. Starting from this time, the residual stresses appear, induced by the chemical shrinkage and thermal expansion. Figure 7 shows the comparison between the yield and residual stresses at the centre of the plate. The evolution of the degree of cure at the centre of the plate is also represented. For the considered case, the residual stress remains below than the resin yield stress experimentally characterized. This means that the residual stress presents before cool-down subsists (no relaxation) in the plate.

Chemical shrinkage effect: The effect of the chemical shrinkage on the residual stresses is pointed out. The curing process of a 10 mm thickness unidirectional plate, subjected to a curing cycle composed of a 3°C/mn heating ramp from 20 to 180°C and a plateau at 180°C during 180 mn, is considered. In this example, only the residual stresses, due to the chemical shrinkage, are examined. The aim is to emphasize the influence of the chemical shrinkage and its anisotropy on the residual stresses. Two cases are considered.

In the first case, the coefficients of chemical shrinkage of the unidirectional composite material in the longitudinal (CCS_1) and transverse (CCS_2) directions are determined by a linear law of mixtures of the resin (CCS^m) and fibers (CCS^f) chemical shrinkages (Eq. 7).

$$CCS_i = (1 - v_f) CCS^m + v_f CCS_i^f \quad (7)$$

with $i=1,2$

It should be noted that the carbon fibers do not undergo a chemical shrinkage: $CCS_i^f = 0$. Since the composite coefficient of chemical shrinkage is directly proportional to the coefficient of the resin, an isotropic behavior is attended.

In the second case, the multi-scale self-consistent model is used and thus an anisotropic chemical shrinkage is taken into account.

A strong deviation is thus observed on the transverse residual stress evolution as a function of time for the two considered cases. In the first case (isotropic shrinkage), the reached values are almost 2.7 MPa at the end of the plateau while in the second case (anisotropic shrinkage), the reached values are around of 0.025 MPa. Even if the values are relatively low, it can be noticed the importance of the chemical shrinkage modeling of the composite material on the estimation of residual stresses. Of course, the anisotropy introduced by the self-consistent formalism should be corroborated by experimental results.

CONCLUSION

An original study of process induced stress in thermosetting composite materials is presented. The presence of this residual stresses through the laminate thickness is proved experimentally. The concept of yield-stress is used as a criterion for the formation and development of residual stresses. The resin yield stress is characterized and its variation with the material state advancement is modeled. The time corresponding to the appearance of a yield stress for the resin is also determined. The residual stresses at the microscopic scale are compared to this resin yield stress to know if a relaxation appears. For the studied case, there is not a release of residual stresses during the curing process before cooling. A future study will be focused on the modeling of the non-linear relaxation of the residual stresses when these stresses become more important than the resin yield stresses. A multi-scale self-consistent model is proposed to calculate the effective mechanical, thermal and chemical properties of composite from the properties of the constituents. This model allows considering an anisotropic chemical shrinkage inducing strong interaction on the process-induced residual stresses. An experimental study is necessary to well improve this anisotropic behavior in chemical shrinkage.

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