THE EFFECT OF DIFFUSION AND PRESSURE ON POROSITY IN COMPOSITES

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Abstract
This work is aimed to the development of a finite element model, able to evaluate the evolution of resin pressure gradient across the laminate as a function of temperature and degree of reaction. This model takes into account viscosity changes, during autoclave cure cycles, and includes kinetic and rheological input parameters experimentally determined by Differential Scanning Calorimetry and rheological analyses. The predicted resin pressure for different lay-up, including peel ply thickness, has been compared with the results of experimental characterization of void evolution measured at different pressures.

1. Introduction

Porosities in composites mainly arise as a consequence of trapped air and water absorbed during prepreg exposure at a humid environment. Processing of aeronautic parts is aimed, among other goals, to minimize these porosities thanks to many mandatory manufacturing procedures involving prepreg cutting, lay-up, vacuum bagging and the curing cycle, the first three performed in a controlled humidity environment. Autoclave curing involves the application of heat and hydrostatic pressure at the external side of the vacuum bag film. The resin temperature and pressure strongly affect the evolution of porosity arising from absorbed water [1-3]. Even if many approaches were devoted to the study of void growth, the key role of resin pressure on the development of porosity is fully recognized. Experimental measurements from Campbell [4] indicated that the hydrostatic pressure in the resin is not necessarily equal to that in the autoclave, since a fraction of the autoclave pressure can be supported by the intrinsic stiffness of the reinforcement stack. This arises as a consequence of a resin flow into the bleeder/breather, which although very limited play a key role in the force balance. This balance must consider a non linear compressive behaviour of the reinforcement as well as the dependence on temperature and degree of reaction of the resin viscosity during a curing cycle [5,6].
In this work, a finite element (FE) model for the evolution of resin pressure gradient across the laminate thickness as a function of temperature and degree of reaction, accounting for viscosity changes during autoclave cure cycles, has been developed. The model improves previous works on composite consolidation, (e.g. Lionetto et al [7]) by also taking into account the variation of pressure across the laminate thickness, thus providing a pressure gradient across the laminate.
The model exploits the general theory of three-dimensional soil consolidation formulated by Biot [8] by considering the particular case of a column of a linear elastic soil supporting a constant perpendicular load and confined laterally in a rigid sheath so that no lateral expansion can occur. It can

be assumed that this simplified case is comparable to the composite consolidation during the autoclave process. On the other hand, the linearity of stress-strain relation does not hold for a prepreg stack under out-of-plane compression, since the reinforcement shows a non linear stress-strain behaviour.

The proposed FE approach also includes a kinetic and rheological model whose input parameters have been previously determined by Differential Scanning Calorimetry and rheological analysis [9]. The predicted resin pressure for different lay up, including breather thickness and for different cure cycles has been compared with the results of experimental characterization of void evolution.

2. Results And Discussion

2.1 Model development

The following equilibrium equation governs the stress during the consolidation of a laminate in the autoclave process [7]:

$$P_{aut} = \sigma + P \tag{1}$$

Where P_{aut} is the external autoclave pressure, P is the resin pressure and σ is the load taken by the reinforcement stack.
Upon heating, the resin viscosity decreases and a pressure gradient is developed across the lay-up.
The resin fills the bleeder thanks to the compaction of the reinforcement: resin flow occurs until the bleeder thickness is filled under autoclave pressure (in plane flow is here neglected). The upper resin layer is under vacuum during bleeder filling. The composite thickness is reduced as the bleeder absorbs more and more resin. During the bleeder filling, the autoclave pressure is sustained either by the reinforcement either by the resin. When the resin fills the bleeder and is in contact with vacuum bag, the flow ends. The pressure is distributed between that supported by the reinforcement, under compressive strain, and the hydrostatic pressure in the resin.

The changes of pressure in the resin and the compression stress taken from the prepreg stack have been modelled exploiting the consolidation theory of soil formulated by Biot [8] and more recently applied by Dave to composite processing [1]. The Biot theory defines the laws for the consolidation of a porous elastic soil containing an incompressible fluid (e.g. water), thus enabling the calculation of the fluid pressure gradient across the soil thickness and the settlement of soils when an external compression force is applied, which causes the water squeezing out of the soil. The main assumptions of the Biot theory are: (1) linearity of stress-strain relations, (2) small strains, (3) the water contained in the pores is incompressible, (4) the water may contain air bubbles, (5) the water flows through the porous skeleton according to Darcy’s law.

By analogy, this theory can be applied to the consolidation of composite laminate during the autoclave process with the appropriate modifications and simplifications. In particular, the prepreg stack that must be consolidated under an autoclave pressure, P_{aut}, can be compared to a column of soil supporting the external pressure and laterally confined in a rigid sheath, so that no lateral expansion can occur. For this case, it can be also assumed that the resin cannot flow laterally (for instance as it can occur in a wide laminate) or through the bottom while it is free to flow at the upper surface by applying the load through the porous bleeder (in plane flow is then neglected).

Another simplification is to compare the prepreg stack to the completely saturated clay of Biot study, involving that the volume change of the composite is equal to the amount of resin squeezed in the bleeder.
The assumptions stated above make the consolidation problem one-dimensional (through the thickness direction) and simplify the Biot's general equations into the equation 2.

$$\frac{\partial}{\partial x}(c\frac{\partial P}{\partial x}) = \frac{\partial P}{\partial t} \quad (2)$$

Taking the x-axis positive downward, the resin pressure P will depend only on the coordinate x and the time t. In eq. 2, c is the consolidation constant and in this case it is given by:

$$c = \frac{k}{\mu * a} \quad (3)$$

Where k is the transversal permeability of the reinforcement, μ is the resin viscosity and a is defined by Biot as the final reinforcement compressibility and is given by eq. (4).

$$a = \frac{1-2\nu}{2G(1-\nu)} \quad (4)$$

Where G is the reinforcement shear modulus and ν is the reinforcement Poisson's modulus.
Equation (2) along with the boundary and the initial conditions leads to a complete solution of the problem of consolidation.
Taking the thickness of the laminate to be h and x=0 at the top (contact with bleeder), the boundary conditions are P =0 for x=0 and $\frac{\partial P}{\partial x} = 0$ for x=h.
The first condition expresses that the pressure of the resin under the load is zero since the resin surface is kept under vacuum until the bleeder is filled. The second condition expresses that the resin cannot flow through the bottom of the tool. The initial condition is P =P_{aut} for t=0.
Unlike the soil studied by Biot, the reinforcement is characterized by the non-linear stress-strain relation, as shown by Lionetto's work [9], where an exponential growth function for the load taken by the reinforcement stack was found (eq 5),

$$\sigma = A_0 e^{\frac{\varepsilon}{A_1}} - A_0 \quad (5)$$

where A_0 and A_1 are parameters of the model and the deformation, ε, is given by the resin flow across the breather. It is possible to calculate the local strain gradient across the laminate thickness, substituting eq. (5) into (1):

$$\varepsilon(x,t) = A_1 \ln\left(\frac{P_{aut} - P(x,t) + A_0}{A_0}\right) \quad (6)$$

The displacement of the laminate is obtained by space integration of eq. 6. In this first approach the temperature across the composite was considered uniform, following the same time dependence according to the cure cycle adopted. The reinforcement permeability is assumed constant, while the viscosity is a function of the temperature, T, and of the degree of reaction, α, so a kinetic and a rheological model must be solved together with eq. 2.
The kinetic and the rheological models were taken from the Lionetto's work [7], and are reported in the equations 8,9.

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^{n1} + k_2\alpha^m (1-\alpha)^{n2} \quad (8)$$

where n1, n2 and m are reaction orders and the kinetic constants ki have an Arrhenius dependence on temperature ki=k0iexp(-Ei/RT) i=1,2. The initial conditions for eq. 8 are α=0 for t=0.

$$\eta = \eta_0 \exp\left[-\frac{C_1(T - T_{g0})}{(C_2 + T - T_{g0})}\right]\left[\frac{\alpha_g}{\alpha_g - \alpha}\right]^{A+B\alpha} \quad (9)$$

where Tg_0 is the glass transition of unreacted resin, α_g the degree of reaction at gel time and η_0, C1, C2, A and B constant parameters.
The model has been applied using the properties of CYCOM 977-2, a toughened epoxy resin produced by Cytec Engineered Materials (formulated for autoclave and press moulding technology), reinforced with a carbon fabric characterized by a high initial Vf, i.e. 57%, (HexForce® G0926 5H satin 370 g/m2 covered by a binder for preforming, provided by Hexcel).
The parameters used in eq. 2, 8 and 9 are reported in Table 1 [7].

Table 1. Model parameters

A_0 (MPa)	A_1	m	n_1	n_2	K_{10} (s^{-1})	E_1 (kJ/mol)	K_{20} (s^{-1})
0.396	0.0325	0.58	0.79	1.99	$1.15*10^{10}$	127.0	140
E_2 (kJ/mol)	η_0 (Pa s)	T_{go} (K)	C_1	C_2 (K)	α_g	A	B
45.12	$6.05\ 10^{10}$	266	34.52	53.09	0.455	6	8

2.2 Model results

Equations 2, 7 and 8 have been simultaneously solved with FlexPDE imposing a temperature program given by a constant heating rate followed by an isotherm at 180 °C (the cure temperature of the resin, as indicated by the manufacturer).
Two case studies have been considered:
-Case 1: thick bleeder (0.5 mm, overbleeding condition);
-Case 2: normal bleeder (0.135 mm).
In the Case 1, a carbon fiber preform of 2 mm thickness, with a bleeder thickness of 0.5 mm under an autoclave pressure of 0.8 MPa was adopted. Figure 1 and 2 show the evolution of the hydrostatic resin pressure, the resin viscosity and the compressive stress in the reinforcement across the laminate thickness as a function of temperature assuming a heating rate of 2 °C/min. The adopted bleeder thickness, being 1/4 of the composite thickness, can be considered a condition of “over bleeding.”

As shown in the figure 3 the prepreg stack under a compression pressure of 0.8 MPa (i.e., the autoclave pressure) cannot be strained more than 0.26 mm, preventing the complete filling of the bleeder. During the flow, the hydrostatic pressure in the resin changes across the thickness and its final value depends on the fraction of pressure taken from the reinforcement stack. As shown in figs. 1 and 2, at temperatures higher than 88.5 °C, autoclave pressure is supported by the elastic reaction of the fiber stack and is not transferred to the resin. The resin pressure becomes zero before the minimum of viscosity is reached, i.e. the resin viscosity is still decreasing and the cure reaction is not yet started. This condition can be highly favourable to the formation of porosities arising from volatiles, mainly water, characterized by a higher vapour pressure as its boiling point is approached.

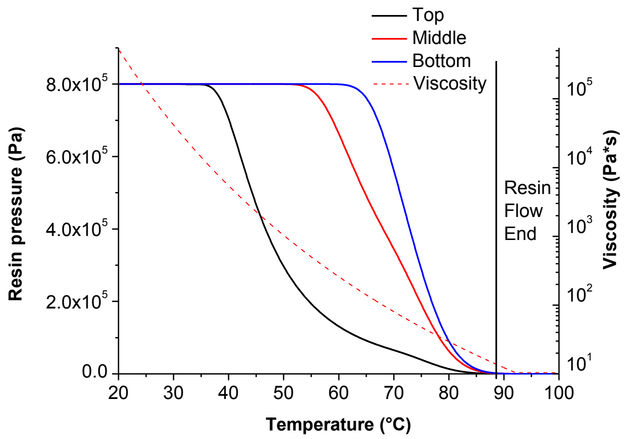

Figure 1. Model results for Case 1:Evolution of resin pressure across the laminate thickness and viscosity

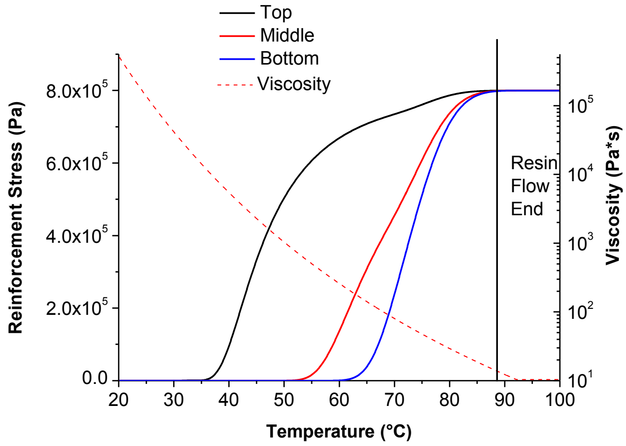

Figure 2. Model results for Case 1:Evolution of reinforcement stress across the laminate thickness and viscosity

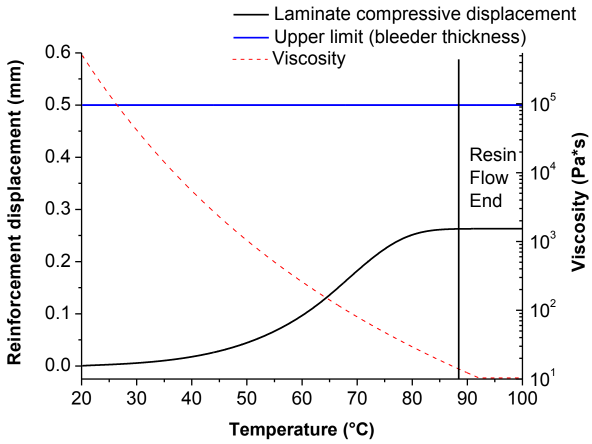

Figure 3. Model results for Case 1:Evolution of reinforcement compressive displacement vs bleeder thickness and viscosity

In the Case 2, a 2 mm thick prepreg stack, with a bleeder thickness of 0.135 mm under an autoclave pressure of 0.8 MPa was adopted. Figure 4 and 5 show the evolution of the hydrostatic resin pressure, the resin viscosity and the compressive stress in the reinforcement across the laminate thickness as a function of temperature assuming a heating rate of 2 °C/min.

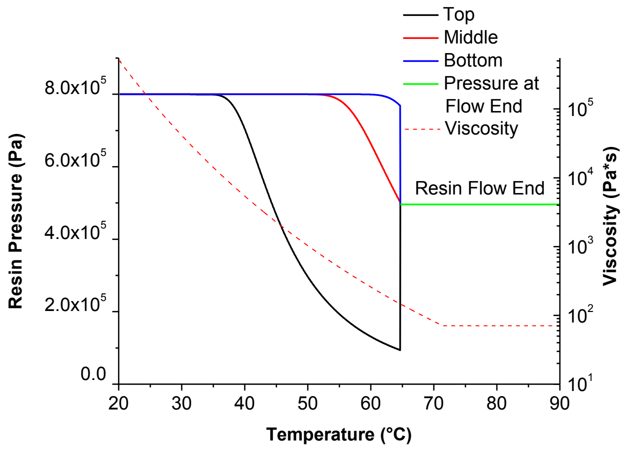

Figure 4. Model results for Case 2:Evolution of resin pressure across the laminate thickness and viscosity

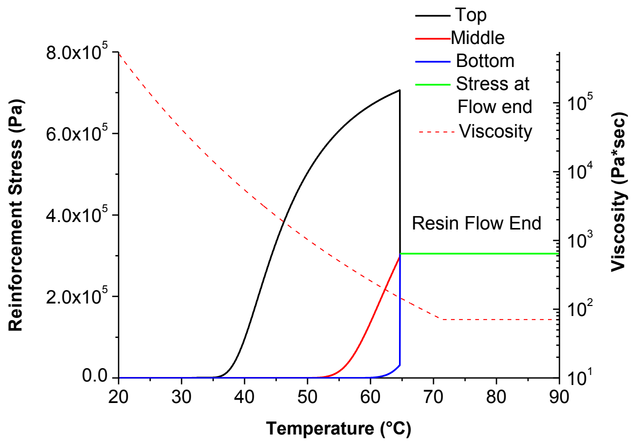

Figure 5. Model results for Case 2: Evolution of reinforcement stress across the laminate thickness and viscosity

In this case, the resin flow ends due the saturation of the bleeder, in fact the fiber stack can be strained under a pressure of 0.8 MPa more than 0.135 mm (figure 6).

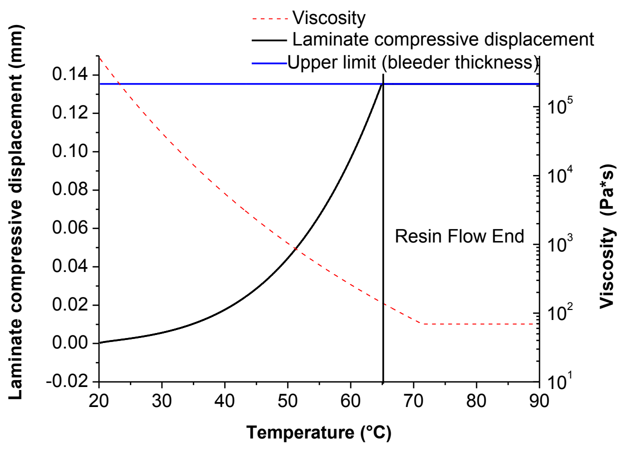

Figure 6. Model results for Case 1: Evolution of reinforcement compressive displacement vs bleeder thickness and viscosity

A fraction of the autoclave pressure is taken by the elastic reaction of the reinforcement and the pressure of autoclave is not completely transferred to the resin across the laminate thickness. At the end of the flow the resin pressure load levels off to 0.49 MPa as shown in figure 4.

The real pressure in the resin could be used as an input for a more complex model accounting for porosity nucleation. The resin pressure will stay at this level, eventually allowing porosity development until gelation is reached.
Preliminary tests carried out on neat resin samples conditioned at different humidity level and cured at different pressures are shown in Fig. 7 under the same curing cycle used in the modelling (i.e. heating at 2 °C/min). The evolution of porosity does depend on the actual hydrostatic pressure in the resin. A minimum resin pressure of 0.4 MPa is apparently needed to prevent porosity nucleation and growth even at high initial humidity content. The occurrence of porosities at a pressure lower than 0.2 MPa in resin samples previously dried suggests that other volatiles can evolve in these conditions.

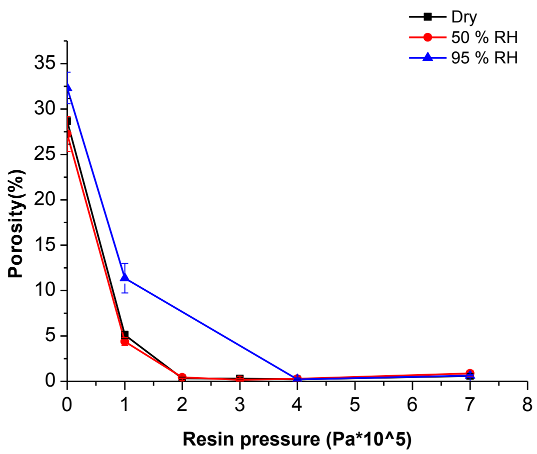

Figure 7. Void content in the studied epoxy resin as function of the hydrostatic pressure. Effect of conditioning at different relative humidity (RH) enviroments.

3. Conclusions

A model capable to predict the pressure changes occurring during an autoclave cycle has been developed. The model takes into account the out-of-plane flow in the breather and simulates the

unreacted prepreg using the Biot consolidation model. Furthermore, a full simulation of the cure behaviour was performed considering the dependence of the resin viscosity from temperature and degree of reaction. The effect of the flow and of reinforcement compression indicates that only a fraction of the autoclave gas pressure is transferred as hydrostatic pressure in the resin.
As a future work, the introduction of an energy balance in the model can be envisaged. The effect of volatile diffusion under vacuum before breather is filled by the resin will be also considered adding a mass balance where the temperature dependence of the diffusion coefficient of water in the resin must be considered. Experiments on resins and prepregs with different content of water and under different hydrostatic pressures will be performed to better validate the model.

Acknowledgments

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