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MODELING OF VOID GROWTH MECHANISMS DURING THE MANUFACTURING OF COMPOSITE LAMINATES

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SUMMARY: Manufacturing composite laminates made of epoxy resin matrix and long carbon fibers is divided into several operations. The most critical one is the cross-linking stage of the thermoset resin. During this phase, uncured prepreg plies' stacking is transformed into a structural laminate by the achievement of a three dimensional macromolecular resin network. A question of matter is the quality of the polymerization process. If not optimized, it gives birth to defects in the bulk material, such as voids. These defects are considered as possible sources of damage in the composite parts. The aim of this work is to model the evolution of void growth processes in thermoset composite laminates. Diffusion phenomena of gas molecules in resin are neglected for the moment, in order to focus on the study of the viscous effects of the polymer on the gas bubbles entrapped in the fluid. After the models are set and validated, an optimization study is proposed to determine the best temperature and pressure cycles in order to minimize the final void radius.

KEYWORDS: void growth, carbon/epoxy composite laminates, model prediction, autoclave

INTRODUCTION

When composite laminate structures made of epoxy resin and long carbon fibers are manufactured in production facilities, the curing step is one of the most critical. In an autoclave and thanks to appropriate vacuum pressure, temperature and hydrostatic pressure cycles, uncured prepreg plies are cross-linked by an exothermic chemical reaction. High-performance structural laminates comply with the requirements of the aeronautical industry. However, the quality of the manufacturing process and more precisely, the quality of the lay-up and polymerisation process is sometimes uncertain. Defects like voids can indeed be detected in the composite parts manufactured.

These voids may cause an important decrease of mechanical properties such as a reduction of the interlaminate shear strength properties [1]. Moreover they can favour damage and crack initiation and propagation. In this study a semi-analytical model of void growth in a viscous resin fluid has been developed in order to optimize the curing process with respect to void apparition and void growth. The final aim is to produce structures with a minimum void rate. After description of the processing parameters used in the simulation, a viscous dynamic model and solution procedure are presented. The last part of the paper describes an optimization study in order to determine the best temperature and pressure cycles to minimize the final void radius.

Main Process Parameters

The goal of the model is to describe the void radius evolution for prescribed curing conditions during an autoclave polymerization process. Conditions corresponding to those usually applied by industry are used and are shown in Fig. 1.

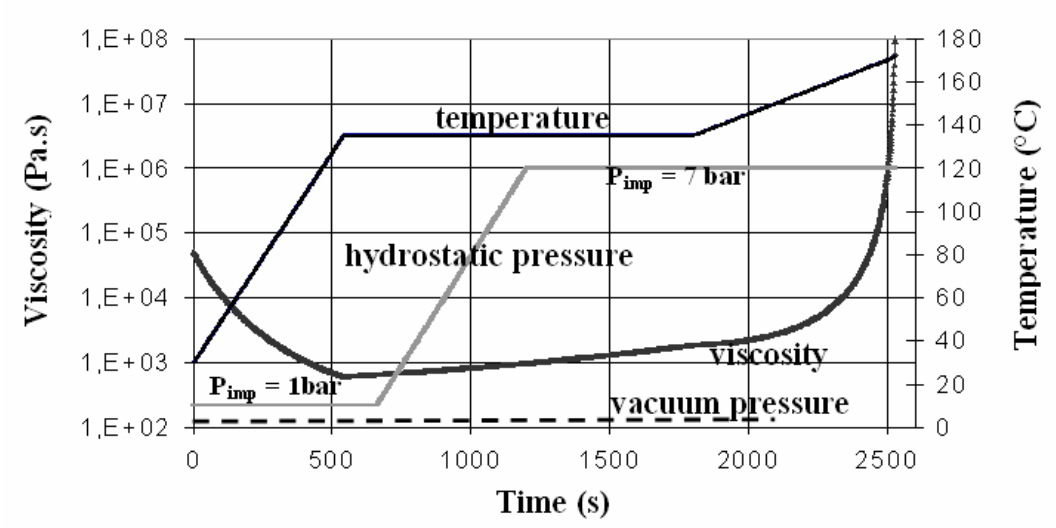

Fig. 1 Typical cure cycle imposed during the autoclave manufacturing process.

As temperature increases, resin viscosity decreases rapidly and chemical reaction begins. Resin viscosity reaches a minimum at about 500 seconds and then begins to increase. Up to this point, little laminate consolidation has taken place other than that associated with inter-plies wetting. During the 135°C temperature hold, an autoclave hydrostatic pressure of 7 bars is applied and laminate consolidation occurs. Resin viscosity was determined as a function of time and temperature in accordance with chemorheological models proposed in literature [2, 3]. More particularly, M. Ivankovic [3] proposed a law, Eqn. 1, obtained empirically for an epoxy anhydride system:

$$\eta(T,\alpha) = \eta_g \exp\left[-\frac{C_1(T-T_{go})}{C_2+T-T_{go}}\right]\left(\frac{\alpha_g}{\alpha_g-\alpha}\right)^a \qquad (1)$$

This model is a combination of the Williams-Landel-Ferry (WLF) equation and a conversion term originally used by Castro and Macosko. Fractional conversion (α) is calculated using modified Kamal and Sourour kinetic model:

$$\frac{d\alpha}{dt} = \left(k_1 - k_2\alpha^m\right)\left(\alpha_{\max} - \alpha\right)^n \text{ with } k_i = k_{io}\exp\left(-\frac{E_{ai}}{R_b T}\right) \quad (2)$$

The thermokinetic model parameters are summarized in Table 1.

Table 1 Parameters of chemorheology model of epoxy resin

Symbol	k_{o1}	k_{o2}	E_{a1}	E_{a2}	T_{go}	η_g	m	n	α_g	α_{max}	C_1	C_2	a
Unit	s^{-1}	s^{-1}	kJ/mol	kJ/mol	K	Pa.s	/	/	/	/	/	/	/
Value	$e^{10.7}$	$e^{12.6}$	61.4	62.1	235.4	10^{17}	0.64	1.36	0.33	-0.6555+0.0035T	36.5	19.6	2.7

Void Growth Model in Viscous Media

A polymer foaming cellular model is used for void growth investigation in viscous media (Fig. 2). This model was largely developed by M. Amon [4]. A gas bubble growing in a thermoset polymer matrix is considered, due to several parameters:

- differential pressure between the imposed pressure P_{imp} and gas pressure in the void P_{gaz},
- gas temperature (T) variation,
- resin viscosity variation during the cure cycle due to the polymer cross-linking.

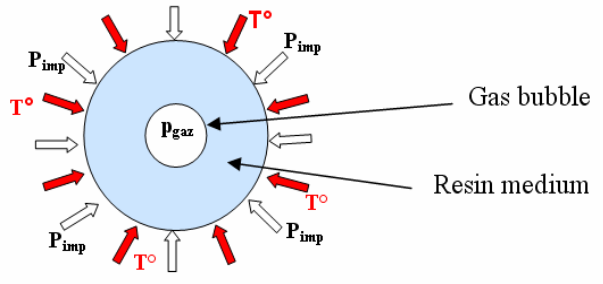

Fig. 2 Schematic of the cellular model.

The following assumptions are made:

a) The void and the thermoset resin are non-miscible. Therefore diffusion phenomena of gas molecules in the resin are not yet taken into account.
b) The void is a sphere of radius R_p.
c) The gas in the void is assumed to be a perfect gas.
d) The thermoset resin is incompressible and Newtonian.
e) Inertia and mass effects are neglected compared to viscous effects and stress due to gas pressure.

The kinematics of spherical bubble growth are ideally described by a purely radial velocity field, which is obtained from the continuity equation. The strain rate tensor, Eqn. 3, is characteristic of a biaxial extensional flow:

$$\underline{\underline{\dot{\varepsilon}}} = \frac{\dot{R}_p R_p^2}{r^3}\begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3}$$

As a consequence the radial component of momentum equations reduces to

$$\frac{d\sigma_{rr}}{dr} + \frac{2}{r}\left(\sigma_{rr} - \sigma_{\theta\theta}\right) = 0 \tag{4}$$

The boundary conditions are described as follows:

$$\begin{cases} \sigma_{rr}(R) = -p_{gaz} + \dfrac{2\gamma_{LV}}{R_p} \\ \sigma_{rr}(+\infty) = -p_{imp} \end{cases} \tag{5}$$

For a viscous liquid resin, the classical Cauchy stress tensor is:

$$\underline{\underline{\sigma}} = 2\eta(T,\alpha)\,\underline{\underline{\dot{\varepsilon}}} - p\underline{\underline{I}} \tag{6}$$

Dynamic viscosity is fitted versus time according to experimental data (Fig. 1). Finally, by expressing gas pressure inside voids thanks to perfect gas law and initial conditions, the following differential equation is obtained:

$$\frac{\dot{R}_p}{R_p(t)} - \frac{p_o \dfrac{T(t)}{T_o}\left(\dfrac{R_o}{R_p(t)}\right)^3 - p_{imp}(t)}{4\eta(T,\alpha)} + \frac{1}{2}\frac{\gamma_{LV}}{\eta(T,\alpha)R_p(t)} = 0 \tag{7}$$

where $\dot{R}_p$ is the void radius growth velocity, γ_{LV} the surface tension and $\eta(T,\alpha)$ the resin viscosity calculated with Eqn. 1. Parameters T_o, p_o and R_o are the temperature, the gas pressure and radius at the initial time t = 0 respectively. Cycle temperature variations are taken into account, but the gas and resin temperatures are assumed to remain equal at each time step.

Results and Discussion

The nonlinear differential equation, Eqn. 7, can be solved using the Runge Kunta 4 implicit scheme implemented in Matlab® software. Autoclave pressure, temperature and gas pressure inside the void are updated at each time step. The range of parameter values considered covers those employed during the industrial manufacturing process of composite laminates (Table 1). R_{max} represents the void radius at t = 600 seconds, when hydrostatic pressure increase begins. R_{final} is the void radius at t = 3000 seconds or when viscosity is over 10^8 Pa.s. In this case, it can be supposed that resin is too viscous to allow growth or shrink of void. Fig. 3 plots the void radius R_p for the processing parameters previously presented in Fig. 1.

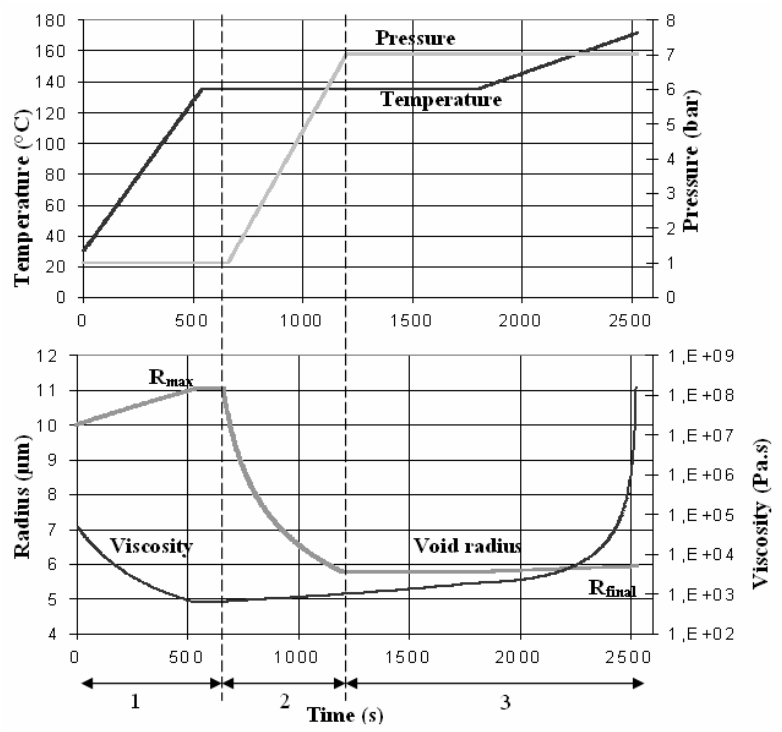

Fig. 3 Void radius, temperature and pressure evaluation with time.

The radius variation can be divided in 3 stages:

- *Stage 1*: under constant pressure but increasing temperature, and decreasing viscosity, the void grows. After 600 seconds, the growth slows down due to the viscosity stabilization and also due to the decrease of the differential pressure between the polymer and the gas inside the void.
- *Stage 2*: the void radius is stabilized due to constant pressure and temperature. After 600 seconds, the hydrostatic pressure is increased from 1 to 7 bars. Moreover, viscosity reaches its minimum value during this stage. Consequently, the void radius is divided by approximately two.
- *Stage 3*: the pressure is constant and viscosity increases exponentially due to the cross-linking of the thermoset resin. A small increase of temperature may induce a small growth of the void.
- *Finally*, after 2500 seconds, the void size is stabilized to 6 µm.

Table 2 Process parameters used in the parametric study

γ_{LV} (Pa.m)	0	0.05	0.5
R_{max} (µm)	11.17	10.84	8.64
R_{final} (µm)	6.04	6.00	5.60
Defaults values: R_o = 10 µm; P_o = 1 bar			

The influence of the surface tension parameter is studied and the results are presented in Table 2. L.E. Scriven [5] mentioned that surface tension effects (γ_{LV}) are neglected since they are only significant during the initial expansion of the void nucleus. Nevertheless, this parameter is

included in Eqn. 7. So its influence is studied with different imposed values from 0 to 0.5 Pa.m: the higher the surface tension, the smaller the final radius. And instead, the results show that the surface tension has trifling effects on the final radius and can be neglected. Then Eqn. 7 becomes:

$$\frac{\dot{R}_p}{R_p(t)} - \frac{p_o \frac{T(t)}{T_o}\left(\frac{R_o}{R_p(t)}\right)^3 - p_{imp}(t)}{4\eta(T,\alpha)} = 0 \qquad (8)$$

Using Eqn. 8, a numerical optimization study can be used to determine more precisely the pressure and temperature cycles with respect to resin viscosity in order to minimize the final void radius.

Optimization Procedure

Aim of the optimization study is to reduce as much as possible the void radius obtained at the end of the polymerization cycle. It is shown previously that this parameter depends on temperature and pressure conditions applied during the curing cycle. So, the values obtained by these two cycles can be modified in order to optimize the final void radius. To this aim, abscises of 3 points on the temperature curve (represented by triangles in Fig. 4) and two points on the pressure curve (represented by squares in Fig. 4) are fixed. The ordinates of the temperature and pressure points can vary between given limits. Indeed, there are 5 optimization parameters represented by the ordinates in temperature and pressure of the 5 points. At each optimization step, the algorithm determines the ordinates for these 5 points. Temperature and pressure cycles versus time are obtained using a cubic fit of the points obtained as explained previously. For each step, the final radius is calculated with these fitted temperature and pressure points. Starting with this radius, the optimization procedure recalculates the 5 temperature and pressure ordinates in order to minimize the final void radius. If a convergence criterion is reached, the procedure is stopped, and optimized temperature and pressure cycles are obtained to minimize the final void radius.

The optimization algorithm has to be chosen carefully. Determinist or stochastic methods such as Monte-Carlo method and genetic algorithms [6] can lead to global minimums, but the objective function requires several iterations to converge. Gradient methods [7] imply the computations of the function gradients, such as in BFGS [8] and Sequential Quadratic Programming (SQP) [9]. The computation of gradients by finite difference methods is time consuming and depends on the perturbed values of process parameters. However, the combination of several methods, particularly when using SQP [10], is considered to be the most stable and efficient way for solving mathematical programming problems with non linear constraints. This algorithm implemented in Matlab® is used to minimize the final void radius by optimizing the temperature and pressure cycles. The results of this optimization procedure are presented in Fig. 4.

The first graph of Fig. 4 describes the new optimized pressure and temperature cycles. Those can be compared with the former ones, plotted with dotted lines, as presented in Fig. 3. In the optimized cycle, the autoclave pressure is imposed later (1500 s) than in the former one. The 135°C temperature hold disappears for the benefit of a small decrease of temperature. This slows down the exponential increase of viscosity as it can be seen in the second graph. This one represents the radius and viscosity as a function of time. Like in Fig. 1, the viscosity attains a

minimum at about 1500 seconds, when the autoclave pressure is applied. After that, the viscosity remains more or less constant until 2600 seconds, and then increases exponentially, due to gelation of the thermoset resin. The void radius reaches a maximum when the viscosity is minimal and decreases after 1500 seconds due to the imposed hydrostatic pressure. The radius is not calculated when the viscosity is over 10^8 Pa.s, because the material is supposed to be too viscous to permit growth or shrinkage of the void. This limit is attained when the fractional conversion (α), calculated with Eqn. 2, is near about the gelation one, α_{gel}, determined empirically. In this case, α_{gel} equals 0,331 as mentioned in Table 1.

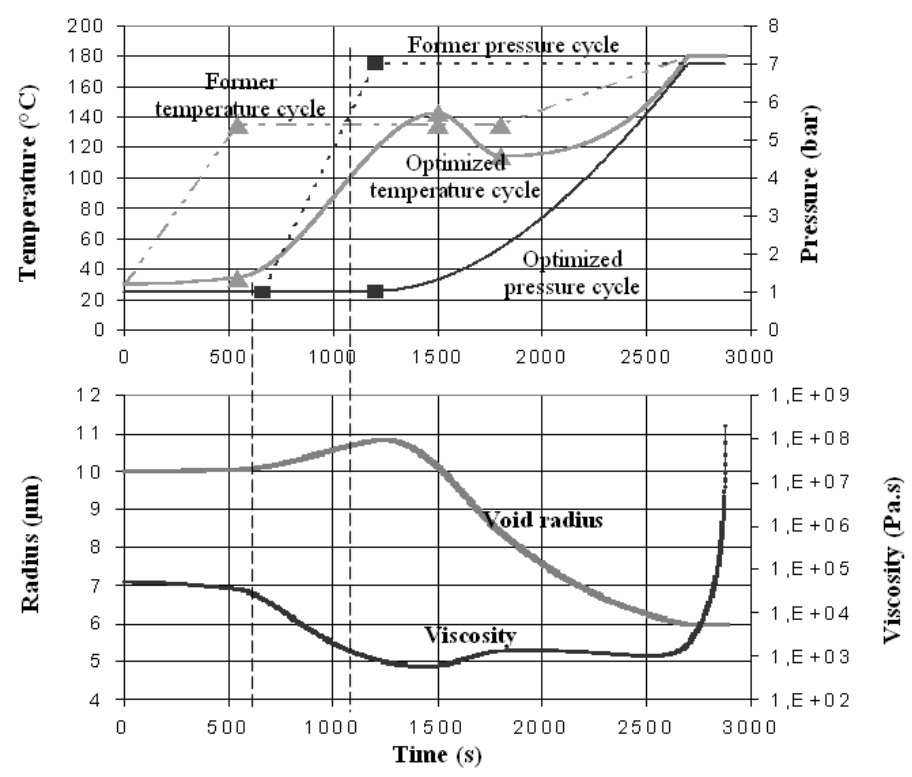

Fig. 4 Void radius and resin viscosity versus optimized temperature and pressure cycle.

Note that the final void radius obtained with the optimized cycles is very close to the one obtained with the traditional temperature and pressure cycles used in industrial field. This remark permits to validate the good agreement between theoretical optimization study and reality. However, optimized cycles are longer than those obtained experimentally by supplier. So, a new optimization study can be investigated with taking into account the time between the beginning and the end of the cycle. The new aims would become to minimize at the same time the final void radius and the curing cycle time. Nevertheless, a new condition can be added in this optimization: in fact manufacturing societies want to obtain composite parts with fractional conversion more than 95%. This means the time of the second temperature hold (180°C) must be considered and calculated to cross link enough composite parts.

Moreover, exothermic phenomena of the resin chemical reaction must not be forgotten when a new polymerization cycle is found, notably for parts thicker than 10 mm. Those phenomena can be taken into account in coupling Eqn. 8 with thermal equations. The same procedure can be

applied to include diffusion phenomena in the optimization study. This also could be the final goal of this work. Model simulation results show that the final void radius is essentially dependant on hydrostatic pressure and resin viscosity which itself depends on temperature and time. Resin-void surface tension seems to have less influence. However, such analytical models need assumptions to find numerical solutions without excessive calculation time. Therefore 3D numerical simulation would have to be carried out in order to obtain results closer to the physical reality. Rem3D®, general 3D polymer injection software, was chosen for this task. It is able to follow the variations of the void radius and other parameters during autoclave processing [11]. This investigation is now under way.

CONCLUSION AND PROSPECTS

The behaviour of a gas bubble in epoxy resin bas been modeled physically considering temperature and pressure conditions applied during autoclave manufacturing typically used in the aeronautic field to cure composite laminates. To this aim, a polymer foaming cellular model in viscous media is implemented. The viscosity variation is predicted with a chemorheological equation developed by M. Ivankovic [3]. This one is a combination of the WLF equation and a conversion term originally used by Castro and Macosko which was verified for epoxy/anhydride system. This model emphasizes the important role of hydrostatic pressure and resin viscosity on the final void size. It is used successfully in the current optimization study to determine the best temperature and hydrostatic pressure cycles which permit to minimize the final void radius. However, the results are obtained by using an important assumption: diffusion phenomena are neglected for instance. Many authors have presented the important relation between void size and absorption or dissolution phenomena which occur during the polymerization stage [12]. Then, the further prospect of this study is to couple our model with the one developed by Kardos et al. [12], in order to improve the prediction of the final void size. In parallel, the optimization study can improve the processing schedule of cure to determine the best cure cycle. Finally, an experimental setup will be designed to measure “in situ” the real void size during autoclave process manufacturing, in order to compare with numerical results.

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