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A 1D COUPLED CURING AND VISCO-MECHANICAL VOID GROWTH MODEL OF THICK THERMOSETTING COMPOSITE LAMINATES

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1. General Introduction

In the production of composite laminate parts, Vacuum Infusion (sometimes referred to as Vacuum Assisted Resin Transfer Moulding (VARTM)) is widely used in the manufacture of large structures such as wind turbine blades [1]. Vacuum infusion is a closed mould process in which resin is pulled into the mould by applying a vacuum at the outlet vent, consequently impregnating dry pre-laid fibres in the mould cavity. Vacuum infusion differs from conventional autoclave-RTM in the sense that no external hydrostatic pressure is applied which helps inhibit void growth during the final consolidation of the resin matrix with the fibres.

It is generally known that voids have a detrimental effect on the strength and fatigue life of composite laminate structures [2, 11]. Several authors have also reported that voids in composite laminates accelerate crack initiation and propagation [3-8]. Liu et al. [2] investigated the void content effect on carbon/epoxy laminate mechanical properties. A decrease of approximately 20% in shear-, flexural- and tensile strength was observed with an increase in void content by approximately 2.6%. Similar tendencies are also observed for the flexural- and tensile moduli as well as the inter-laminar shear strength (ILSS). The mean decrease in ILSS was estimated to average 6% per unit volume of void ratio for carbon/epoxy laminates [15]. Boey & Lye [11] investigated void reduction in processing of thermoset composites. Using vacuum bagging alone, a reduction of the void content below 10% was not possible without applying an external pressure, as done in autoclave processing, where a void content below 3% is possible due to the imposed hydrostatic autoclave pressure before final resin curing.

2. Void growth models

Several void growth models for composite laminates exist, e.g. [7-8],[10]. Kardos *et al.* [10] presented a general time-dependent diffusion-controlled void growth model as well as a model of the void stability at equilibrium as a function of pressure and temperature. Ledru *et al.* [8] presented a coupled visco-mechanical and diffusion model to predict the final void size at the end of polymerization. In their model the resin cure cycle viscosity variation, as a function of temperature and cure degree is taken into account, as well as the process- and gas void pressure difference and gas temperature variation for a unit cell spherical void.

3. Model Formulation

An extension of the 1D thermomechanical model presented by Bogetti & Gillespie [9], based on incremental elastic classical laminated plate theory, is employed to include void growth during VARTM, disregarding resin flow. A visco-mechanical void growth model is implemented, presented by Ledru *et al.* [8] and adapted from Wood & Bader [13] and Kardos *et al.* [10]. Void growth will follow perfect gas law behaviour without taking transport of species across the void/resin interface into account. As a novelty, this is implemented using the finite volume method with a through-thickness spatial domain discretization of the laminate. The model is programmed numerically in Matlab®.

3.1 Main model assumptions

- Constant isotropic thermal material properties are assumed
- Voids are assumed to be initially present in resin after infusion as a result of gas bubbles being trapped in the inter-rovings spaces

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- An initial mean void radius (R_o) and distribution is assumed through the laminate thickness
- The gas void is assumed to be perfectly spherical
- The perfect gas law applies for describing the gas inside the void
- No diffusion takes place, i.e. void and resin are assumed to be non-miscible.

3.2 Thermal model

The governing equation utilized is Fourier's heat conduction equation, reduced to one-dimension:

$$\rho c_p \frac{\partial T}{\partial t} = k_z \left(\frac{\partial^2 T}{\partial z^2} \right) + \dot{q} \quad (1)$$

for $T(z, t)$ in $0 < z < h$ the laminate thickness, and where k_z , ρ and c_p are the through thickness thermal conductivity, density and specific heat capacity respectively. \dot{q} is the heat source term, which in this case represents the exothermic heat generation rate during resin polymerization. The laminate is discretized through the thickness with the surface control volume (CV) being prescribed the imposed process cycle temperature. The remaining CVs experience temperature change due to the combined effect of curing and conduction. In this work symmetric thermal loading is considered, why only half of the laminate thickness is modelled.

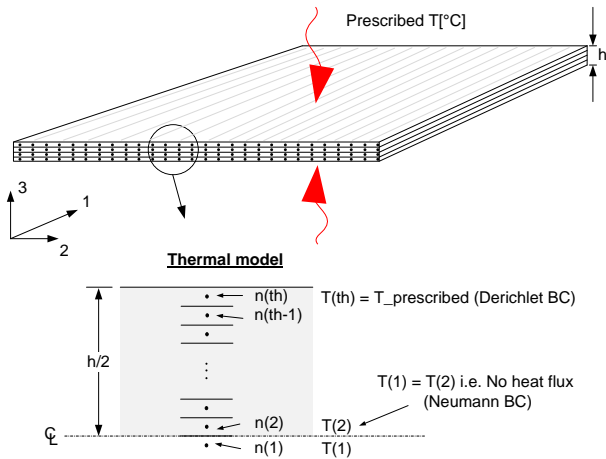


Fig.1. Thermal model discretization and boundary conditions.

The thermal model is discretized spatially in a finite volume framework with a backward Euler finite difference time discretization, see e.g. [17] for details. The resulting equation system is solved implicitly in each time step with Neumann and Dirichlet boundary conditions (BCs) at the centreline and laminate surface boundary respectively see Fig.1.

3.3 Cure kinetics and viscosity

The curing process of thermosetting epoxy resins is exothermic - a result of the drop in energy of the chemical system during polymerization. The degree of cure $\alpha(t)$, at a material point is expressed as the ratio of the cumulative mass specific heat liberated from the chemical reaction, $H(t)$, to the total heat of the reaction H_r . This is expressed as:

$$\alpha(t) = \frac{H(t)}{H_r} \quad (2)$$

The heat liberated at any point in time t is expressed in integral form as:

$$H(t) = \int_0^t \frac{1}{\rho} \left(\frac{dq}{dt} \right) dt \quad (3)$$

Where dq/dt is the volume specific rate of heat generation (or \dot{q}) from the cure reaction. Using (2-3) the heat generation rate in eq.(1) is expressed as a function of the cure rate:

$$\dot{q} = \frac{d\alpha}{dt} \rho H_r \quad (4)$$

The cure rate of epoxy resins can be expressed (depending on the resin system) using the Kamal and Sourour kinetic model [14]:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (5)$$

$$\text{with } k_i = k_{i0} \exp\left(-\frac{E a_i}{R_b T}\right) \quad (6)$$

The degree of cure is calculated from 0 to 1, where 1 is fully cured. The resin rheology is modelled via the viscosity being a function of temperature and cure

Table 1. Epoxy thermal and cure kinetic parameters

Notation	c_p	k_z	α_{CTE}	k_{o1}	k_{o2}	E_{a1}	E_{a2}	H_r	m	n
Unit	J/W.K	W/m.K	$^{\circ}\text{C}^{-1}$	s^{-1}	s^{-1}	kJ/mol	kJ/mol	kJ/kg	-	-
Value	942	0.2163	5.7E-5	1528	1.6	59.4	26.3	198.9	0.51	1.49

degree using:

$$\eta(T, \alpha) = \eta_g \exp \left[-\frac{C_1 (T - T_{go})}{C_2 + T - T_o} \right] \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^a \quad (7)$$

which is a combination of the Williams-Landel-Ferry (WLF) expression and the Castro and Macosko conversion term. η_g is the resin viscosity at gelation, C_1 and C_2 are model parameters and α_g is the crosslinking ratio at gelation. A viscosity limit of 10e6[Pa s] is used, corresponding to solidification of the resin [15].

3.4 Void growth in viscous media

The void growth model used is largely developed by Amon and Denson [16]. The model entails a spherical gas bubble developing in a polymer matrix, see Fig. 2. A spherical gas void is studied. The bubble size variation is described using the radial velocity component only ($v = [u, 0, 0]^T$) due to isotropic growth or contraction.

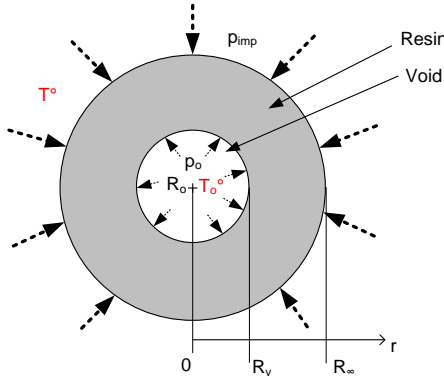


Fig.2. Schematic of gas bubble surrounded by resin with imposed pressure and temperature.

Using the standard strain-displacement relations in spherical coordinates as well as incompressibility, the strain rate tensor is given as:

$$\underline{\underline{\dot{\epsilon}}} = \frac{\dot{R}_v R_v^2}{r^3} \begin{bmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (8)$$

where \dot{R}_v is the void growth velocity. Taking the strain rate tensor into account, the equilibrium equations are hence:

$$\begin{cases} \frac{\partial \sigma_{rr}}{\partial r} + \frac{1}{r} [2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\phi\phi}] = 0 \\ \sigma_{\theta\theta} = \sigma_{\phi\phi} \end{cases} \quad (9)$$

The boundary conditions at the limits (see Fig.1) are:

$$\begin{cases} \sigma_{rr}(R_v) = -p_g + \frac{2\gamma_{LV}}{R_v} \\ \sigma_{rr}(R_\infty) = -p_{imp} \end{cases} \quad (10)$$

which are found using Laplace-Young relationship where surface tension forces γ_{LV} are taken into account as well as the internal void gas pressure p_g and imposed hydrostatic pressure p_{imp} . In the case of vacuum infusion, no external hydrostatic pressure is applied in which case p_{imp} corresponds to atmospheric pressure. Finally, the polymer resin behaviour is assumed to exhibit Newtonian behaviour expressed via the Cauchy tensor as:

$$\underline{\underline{\sigma}} = 2\eta \underline{\underline{\dot{\epsilon}}} - p \underline{\underline{I}} \quad (11)$$

Inserting (8) in (11) we get:

$$\begin{cases} \sigma_{rr} = -4\eta \frac{\dot{R}_v R_v^2}{r^3} - p_{imp} \\ \sigma_{\theta\theta} = \sigma_{\phi\phi} = 2\eta \frac{\dot{R}_v R_v^2}{r^3} - p_{imp} \end{cases} \quad (12)$$

Considering initial pressure, temperature, radius and viscosity conditions, from the presented equations (inserting (12) in (9)) the following differential equation is obtained:

$$\frac{\dot{R}_v}{R_v(t)} - \frac{p_g(t) - p_{imp}(t)}{4\eta(T, \alpha)} + \frac{\gamma_{LV}}{2\eta(T, \alpha)R_v(t)} = 0 \quad (13)$$

where the void gas pressure p_g at time t is:

$$p_g(t) = p_o \frac{T(t)}{T_o} \left(\frac{R_o}{R_v(t)} \right)^3 \quad (14)$$

p_o , T_o and R_o are the initial void pressure,

Table 2. Epoxy resin viscosity parameters and initial void settings

Notation	η_g	T_{go}	C_1	C_2	α_g	a	R_o	p_o	T_o	γ_{LV}	ρ
Unit	Pa.s	K	-	-	-	-	μm	Pa	$^\circ\text{C}$	Pa.m	kg/m^3
Value	10e12	235	29.9	30.0	0.345	2.1	10	1.1e5	30	0.05	1280

temperature and radius respectively. The 1st order non linear differential equation (13) is solved implicitly in each finite volume in each time step but close attention should be paid when determining the roots. Once the viscosity limit of 10e6[Pa s] is reached during solidification, it is assumed that the void size follows the thermal strain of the resin, governed by the resin coefficient of thermal expansion α_{CTE} and the variation in temperature and radius from this point on.

$$R_v(t) = R_{v@ \eta^{max}} + R_{v@ \eta^{max}}(\alpha_{CTE} \Delta T) \quad (15)$$

where $R_{v@ \eta^{max}}$ is the void radius when the viscosity limit is reached and ΔT is the temperature variation after this point.

4. Results

A 40.0[mm] thick glass/epoxy laminate plate is modelled. The model material parameters used are summarized in Table 1 and 2. In Fig. 3 the temperature cycle at the laminate surface as prescribed in the model is seen. The temperatures at the laminate thickness centre and between the centre and surface (quarter) are also seen. The temperature peaks at app. 3000 and 9000[s] represent the exothermic heat generation during polymerization which causes a rise in temperature due to poor material conductivity, i.e. more heat is generated than can be conducted away from the source.

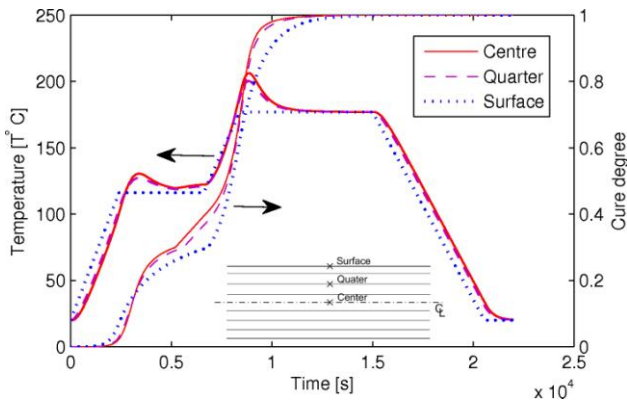


Fig.3. Temperature and cure degree at different thickness intervals during the cure cycle.

Also seen in Fig. 3 are the calculated cure degrees at the same regions (surface, quarter and centre). Notice that it is the centre of the laminate that fully cures first. The resin viscosity development is

similarly seen in Fig.4. Initially, the resin viscosity drops due to the increase in temperature. As polymerization proceeds, so too does the viscosity. The programmed viscosity limit of 10e6[Pa s] is obtained at the centre of the laminate first - a result of the high curing rate here.

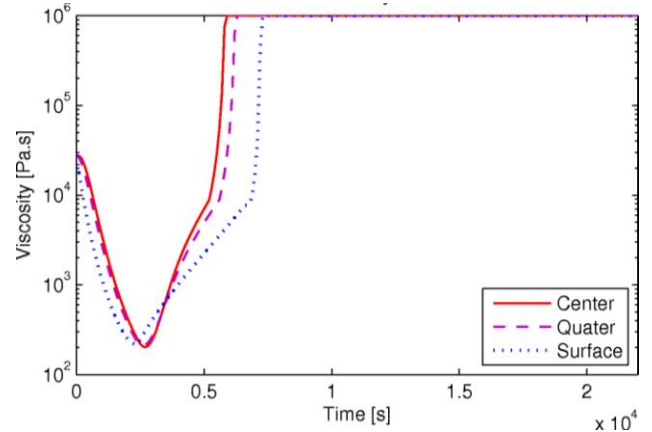


Fig.4. Viscosity development of epoxy resin during the cure cycle.

The non-isotropic through-thickness temperatures and cure degrees drive the non-uniform growth of voids resulting in a non-isotropic through-thickness void diameter as seen in Fig.5. As the resin is not fully cured at the laminate surface after approximately $t=5000$ [s], only an increase in void radius is experienced here due to the second temperature ramp starting at time $t=6600$ [s]. It can be said that the main contribution to the increase in void radius is the initial increase in temperature before the first dwell.

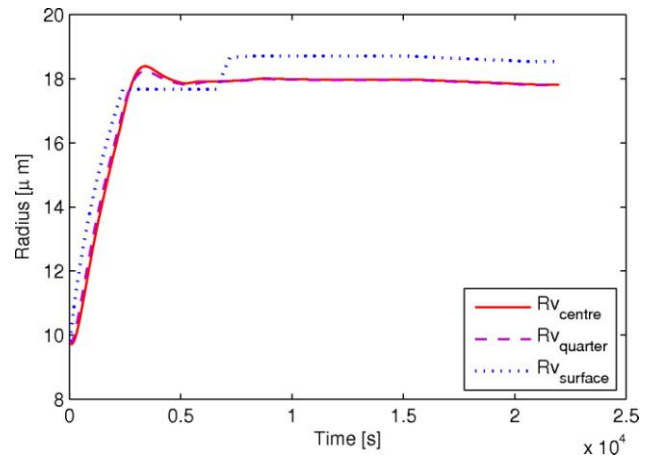


Fig.5. Void radius development during the cure cycle.

A parameter study is conducted to investigate the influence of the initial laminate thickness on void growth. A similar cure cycle as seen in Fig.3 ($T_{surface}$) is prescribed laminates of different thicknesses as this is known to influence the temperature peak during the curing exothermic reaction. In Fig. 6 the final void size variation across the laminate thickness is depicted. It is seen that the thicker laminates exhibit a larger variation in void size through the thickness, although still relatively small, as is expected due to larger through-thickness temperature and cure degree gradients during the cure cycle. Also noticeable is the change in the parabolic-shaped profile, seen for the 20 and 30[mm] laminates, to a W-shaped reversed parabolic profile within the centre for the 40 and 50[mm] laminates. This reversal in the parabolic profiles for thicker laminates is also seen when modelling in-plane residual stress development (see [9]) and is caused by changing from a nearly uniform outside-to-inside cure history for thinner laminates to an inside-to-outside cure history for thicker thermosetting laminates.

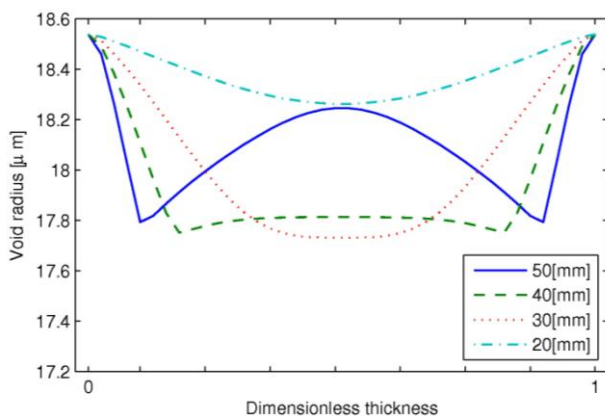


Fig.6. Laminate thickness influence on final void size distribution.

A better understanding of the void radius variations at the centre of the laminates is also gained when analyzing the void radius and viscosity during the entire cure cycle, presented in Fig.7. A higher void radius peak is achieved for thicker laminates due to higher peak temperatures at the centre of the laminate during polymerization, as seen in Fig.7(a). This higher peak is caused by a higher cure rate making a larger part of the curing phase take less time. This is also seen in the earlier occurring abrupt

increase in viscosity for the thicker laminates, as seen in Fig.7(b). This alone is not necessarily an unwanted effect when purely considering the void size. As the 20[mm] laminate takes a longer time to cure, seen in Fig. 7(b) by the late increase in viscosity compared to the thicker laminates, this allows a final increase in void radius to take place due to the second cure cycle temperature ramp up, seen in Fig. 7(a) after approximately 6600[s]. Essentially this indicates that the choice of cure cycle temperature (either from a heated mould or oven) should be chosen with care so as to minimize void growth during curing by allowing a specific increase in resin viscosity before the final temperature ramp up that is normally used to fully consolidate the matrix material.

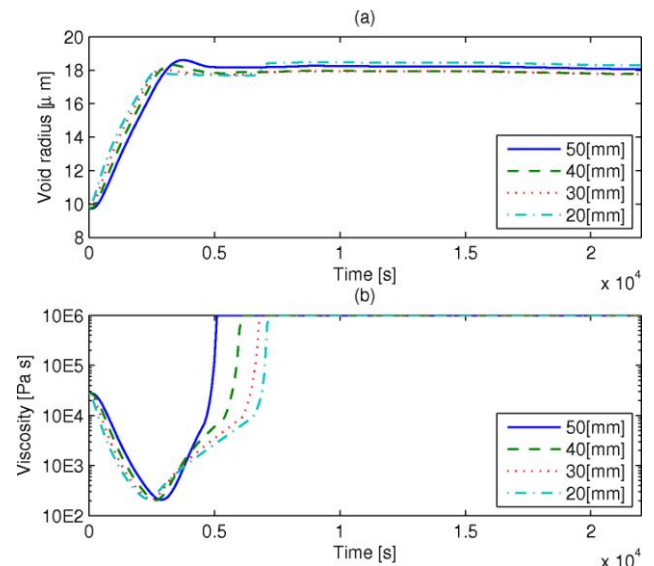


Fig.7.(a) Void radius development at laminate centre during cure cycle as a function of laminate thickness, (b) resin viscosity development for same case

5. Conclusion

In the present work, a model for predicting void growth and void size distribution in a composite laminate through-thickness direction is presented. The model is based on a coupled curing visco-mechanical void growth model mainly based on perfect gas law behaviour. The variation in void size across the laminate thickness is dependent on processing parameters as well as initial laminate thickness. It is known that non-uniform heating and curing can have an effect on the presence of defects, shape and load carrying capacity of a laminate. This

A 1D COUPLED CURING AND VISCO-MECHANICAL VOID GROWTH MODEL OF THICK THERMOSETTING COMPOSITE LAMINATES

is also true for void growth, as approximated by this visco-mechanical model. Specifically it is found that variations, although still relatively small, in final void size distribution through the laminate thickness is seen in thick laminates, as a result of larger gradients in temperature and curing during processing. Furthermore, selecting an appropriate temperature cycle can help minimize void growth, by suiting the temperature ramps and dwells to the laminate thickness, curing behaviour and viscosity.

Of interest in future work is the inclusion of diffusion in the voids growth model. A non uniform distribution of initial void radii through the thickness as well as non-symmetric heating is also of interest to capture non-uniform process-induced effects. Essentially the model can be used in the prediction of process induced effects and their influence on the in-service mechanical performance of large composite parts manufactured using vacuum infusion.

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