Analysis of the Chemical Vapor Infiltration Process: Upper and Lower Bounds for the Void Fraction

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Abstract: A model for Chemical Vapor Infiltration is analyzed. Consider a cylindrical pore with a reacting gas and a non-reacting carrier gas flowing in on the left. The gas reacts with the interior of the pore and the result is a solid matrix. The model assumes that the flux due to binary diffusion is negligible. The model also assumes that the reactions are first order. The results yield mathematical estimates for the concentration and void including upper and lower bounds for the void fraction.

Key–Words: Chemical Vapor Infiltration, CVI, Void Fraction, Mathematical Model

1   Introduction

Consider a porous preform, (*e.g.* fibers, or particles) and a vapor flowing into the preform on one side. The fluid consists of a carrier gas that is non-reacting and a reactant that bonds with the interior surfaces of the preform. The result of the reaction is the deposition of a solid matrix phase that decreases the void of the preform. The void of the preform may continuously decrease until the void at the inlet is zero and no more fluid can enter the solid. At this time the process ends. It is usually desirable that the voids in the preform are minimized and the solid is uniform before the process ends. Since Chemical Vapor Infiltration (CVI) often takes an extremely long time, it is also important to choose parameters that achieve the requisite amount of solid formation in the minimum amount of time.

The process involves several parameters: temperature, pressure, initial void of the preform, chemical composition, chemical concentration etc. An accurate mathematical model is necessary to inexpensively and effectively optimize the process.

A process is successful if the remaining voids in the matrix are within some tolerance. The tolerance is determined by the application of the material. The conclusions that follow can be used to choose the values of the parameters that will yield a successful process. Specifically, the individual processing the composite material can use these results to adjust the controls on a CVI reactor and produce a successful product.

In the research presented here the parameters α^2 (proportional to the reaction rate divided by the diffusion rate) and β (proportional to the reaction rate) are constant during each process. The reaction and diffusion rates are assumed to be a fuction of temperture and pressure. Thus, constant α and β corresponds to an isothermal-isobaric process.

The formulation yields a coupled system of Partial Differential Equations (PDEs) for the void fraction of the preform and the concentration of the reacting gas. Mathematical analysis is used to give approximate solutions to the PDEs as a function of space and time. The properties of the solutions, the void fraction and the concentration, are derived and are in ageement with intuition and experiment. These results can be used to determine sufficient conditions for a successful process.

2   Formulation[†]

A mathematical description of infiltration requires one or more partial differential equations which describe the evolution of the matrix (i.e., the solid phase), and at least one additional partial differential equation for each chemical species in the fluid phase. For a simple pore structure, the continuity equation for species i is

$$-\frac{\partial(\varepsilon C_i)}{\partial t} = \nabla \cdot N_i - \sum_{r}^{n_r} \nu_{ir} R_r \qquad (1)$$

where t is time, ε is the void fraction of the media, C_i is the concentration of species i, n_r is the number

of the gaseous species, ν_{ir} is the stoichiometric coefficients for the ith gaseous species in the rth reaction, and R_r represents the volumetric reaction rate of reaction r.

The basic partial differential equation(s) which describe reaction and mass transport in porous media (i.e., the fluid phase) are well established [Aris (1975);Dullien (1979)]. The Dusty-Gas model [Mason and Malinauskas (1983)] describes multicomponent diffusion and convection. Neglecting thermal diffusion, the relationship between the molar fluxes, N_i, is given by [Jackson (1977)]:

$$\frac{N_i}{D_{K_i}} + \frac{RT}{P} \sum_{j \neq i} \frac{C_j N_i - C_i N_j}{\mathcal{D}_{M_{ij}}} = -\nabla C_i - \frac{C_i B_e}{\mu D_{K_i}} \nabla P$$

(2)

where B_e is the permeability of the porous media, μ is the viscosity of the mixture, and P is the total pressure. $\mathcal{D}_{M_{ij}}$ and D_{K_i} are the effective binary diffusivity for species i and j and the effective Knudsen diffusivity of species i, respectively.

The change in the solid structure is equivalent to considering the change in the void fraction, ε (i.e., the volume fraction of gas inside of the porous solid). The evolution of ε is given by:

$$\frac{\partial \varepsilon}{\partial t} = -uS_v(\varepsilon)$$

(3)

where u is the rate at which the solid product grows (volume/area/time) and $S_v(\varepsilon)$ is the surface area per unit volume of the porous solid.

The simplest formulation for the fluid phase is obtained by considering one reacting species and no pressure gradient. That is, we assume $i = j$ and $\nabla P = 0$ in (1.1.2). Thus, for highly diluted reactant systems in one dimension, the Dusty-Gas model can be simplified to give the following approximate expression for the flux:

$$N = -D_K \frac{\partial C_i}{\partial Z}$$

(4)

where C is the concentration of diluted species and Z is the distance into the preform. The effective diffusivity of the diluted species, D, can be expressed as

$$D = \frac{\varepsilon}{\theta} D_{Mm} \left[1 + N_k(\varepsilon)\right]^{-1}$$

(5)

where m refers to the bulk species, D_{Mm} is the binary diffusion coefficient for M in m, N_k is the ratio of the Knudsen diffusion coefficient and D_{Mm}, and θ is the tortuosity factor. For a diffusion-limited process in one spatial dimension, using Eq. (4), Eq. (1) becomes:

$$\frac{\partial(\varepsilon C_i)}{\partial t} = \frac{\partial}{\partial Z}\left[D_K \frac{\partial C}{\partial Z}\right] - \frac{uS_v(\varepsilon)}{V_M}$$

(6)

where V_M is the molar volume of the solid product. The last term in Eq. (6)

$$\frac{uS_v(\varepsilon)}{V_M} = \sum_r^{n_r} \nu_{ir} R_r$$

describes the rate at which the gas-phase precursor is consumed or created by chemical reactions inside of the pores with the assumption that there are no homogeneous gas-phase reactions.

Are assumption, that there are no gas phase reactions is based on the following. If the gas inlet is a large distant from the sample many gas phase reactions will occur before the gas reaches the first pore. We assume that the gas that reaches the pore is in equilibrium with 44 species of hydrocarbons. The reaction rate of the gas with the surface is taken to be the average of the reaction rates of 44 gasses.

A specific CVI model requires expressions for u, S_v, and D. Our objective in this work is to use simple formulations for each, as a basis for assessing the general behavior of infiltration problems. As an example, consider the formation of carbon matrix composites using a hydrocarbon in an argon carrier gas, where the following net reaction occurs:

$$C_m H_n \text{ (g)} \longrightarrow \text{m } C\text{(s)} + \tfrac{1}{2} \text{ n } H_2\text{(g)}$$

(7)
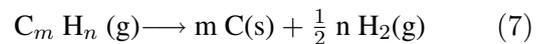
The form of Eq. (6) is based on the assumption that the hydrocarbon concentration, C_r, is dilute (i.e., the reactant concentration is much smaller than the carrier gas concentration). If the carbon growth rate is proportional to the precursor concentration, then:

$$u = kC_r$$

(8)

where k is the reaction rate constant.

The preforms used for CVI typically have a complex porous structure. However, a cylindrical pore is used to formulate simple models. The following expresses the surface area of a circular cylinder S_v as a function of the void fraction:

$$S_v(\varepsilon) = \frac{2\sqrt{\varepsilon_o}\sqrt{\varepsilon}}{r_o}$$

(9)

where r_0 is the initial pore radius and ε_o is the initial void fraction of the preform.

We neglect the change in the number of molecules in the gas phase

$$\frac{\partial(\varepsilon C_i)}{\partial t}$$

This is assumed because solids are much denser than gases, so that the time-scale for changes in the

gas profile is much shorter than the time scale associated with changes in the solid structure. The temporal change is given by (3). For gas-solid reaction processes such as CVI, this is sometimes referred to as the pseudo-steady-state approximation [Chang (1995)]. Transforming ε to η simplifies equation (10). Since η is proportional to S_v, it is also possible to view η as a dimensionless surface area per volume.

Substituting Eqs. (8) and (9) into Eqs. (3) and (6) gives the following forms:

$$\frac{\partial \eta}{\partial t} = -\frac{1}{2}\beta c \qquad (10)$$

$$\frac{\partial}{\partial z}\left[\frac{\eta^2}{\theta}\left[1 + N_k(\eta)\right]^{-1}\frac{\partial c}{\partial z}\right] = \alpha^2 \eta c \qquad (11)$$

where:

$$\eta = \sqrt{\varepsilon}$$

$$c = \frac{C_r}{C_o} \ \text{and} \ z = \frac{Z}{L}$$

$$\alpha^2 = \frac{2k\sqrt{\varepsilon_o}L^2}{V_M r_o D_{Mm}}$$

$$\beta = \frac{2k\sqrt{\varepsilon_o}C_o}{r_o} = \alpha^2 \frac{V_M C_o D_{Mm}}{L^2}$$

where L is the thickness of the preform and C_o is the concentration of the reactant species in the bulk gas-phase (i.e., outside of the preform). The expression for α is based on the assumption that u is determined by a first order reaction, where k is the rate constant (i.e., $u = kC_r$). Note that α^2 is dimensionless and that β has units of inverse time.

The parameters α^2 and β depend on the three key process variables: T (temperature), P (pressure), and C_o (initial concentration). T, P do not appear explicitly in the espressions for α and β, however, k typically obeys an Arrhenius-type exponential temperature dependence, and D_{Mm} varies with both temperature and pressure.

The boundary conditions that are most often used for CVI models are to fix the concentration at the left surface (the inlet) of the preform at C_o:

$$c(0, t) = 1$$

and to assume that the flux at the right surface (i.e., at $z = 1$) is proportional to the concentration:

$$c_z(1, t) = -Ac(1, t)$$

where A is the constant of proportionality. The initial condition is given by:

$$\varepsilon(z, 0) = \varepsilon_o$$

During CVI, the infiltration kinetics are controlled by diffusion and the deposition reaction. To achieve relatively uniform infiltration, diffusion must be fast relative to the deposition rate. This is typically accomplished by choosing processing conditions that result in a slow deposition rate, which usually leads to long infiltration times. Thus, a key processing objective is to obtain the desired amount of infiltration in the shortest possible time. The total amount of infiltration in the preform is given by integrating over z:

$$\bar{\varepsilon}(t) = \int_o^1 \varepsilon(z, t)dz$$

Since it is important to obtain the desired density (i.e., void fraction), ε_f, in the shortest possible time, the optimization problem of interest corresponds to determining the shortest time where $\varepsilon(t) = \varepsilon_f$, for values of ε_f that are significantly smaller than ε_o.

3 Mathematical Analysis

If $f(\eta) = \frac{\eta^2}{\theta}\left[1 + N_k(\eta)\right]^{-1}$ then equations (10) and (11) become

$$\frac{\partial \eta(z, t)}{\partial t} = -\frac{\beta}{2}c(z, t) \qquad (12)$$

$$\frac{\partial}{\partial z}\left\{f[\eta(z, t)]\frac{\partial c(z, t)}{\partial z}\right\} = \alpha^2 \eta(z, t)c(z, t) \quad (13)$$

We subject (12) and (13) to the boundary conditions

$$c(0, t) = 1 \qquad (14)$$

$$\frac{\partial c}{\partial z}(1, t) = -Ac(1, t) \qquad (15)$$

and the initial condition

$$\eta(z, 0) = \eta_0 \qquad (16)$$

where η_0, the initial value of the square root of the void fraction, is constant in space

$f[\eta(z, t)] = \frac{\eta^2}{\theta}\left[1 + N_k(\eta)\right]^{-1}$ and $\frac{f(\eta)}{\eta}$
are both C^∞ monotonically increasing functions of η, and $\eta(z, t)$ is positive for a cylindrical pore

$$\theta = 1 \ \text{and} \ f(\eta) = \frac{1}{3}\frac{\rho\eta^3}{\rho\eta + 1.5410^{-5T}}.$$

That is the diffusivity (cf equ 5)is a function of the shape of the pore, θ, the size of the pore, η and the temperature T.

Assume that α and β are positive and constant with time and space. Physically, this corresponds to an isobaric-isothermal process.

Throughout the process the concentration of the reactants will be held constant on the left-hand surface of the matrix, i.e. $c(0, t) = 1$.

$$\frac{\partial c}{\partial z}(1, t)$$

is proportional to the flux of reactants out of the porous solid. Previously [1], the analysis was done for the case when $A = 0$, *i.e.* the net flux leaving the region [0,1] was negligible. It will be shown that the case when $A = 0$, is optimum for minimizing the infiltration time.

This paper introduces the case when $A > 0$. The solid is not sealed on the right-hand surface so that the carrier gas can escape the matrix. We assume that some of the reactant is going to escape with the carrier gas. Hence $A > 0$ more accurately models the physical flow for this type of process.

The following notation is employed:

$$\gamma^2(z, t) = \frac{\eta(z, t)}{f[\eta(z, t)]}\alpha^2$$

and the subscript zero will denote initial time, *e.g.*

$$\eta_0 = \eta(z, 0).$$

3.1 Properties

In Lemma (2.1), we show that there is an explicit solution for the initial concentration.

Lemma 1 *The initial concentration, $c(z, 0)$, is given by*

$$c(z, 0) = \frac{\gamma_0 \cosh \gamma_0(1 - z) + A \sinh \gamma_0(1 - z)}{\gamma_0 \cosh \gamma_0 + A \sinh \gamma_0}$$

Proof

When $t = 0$, equation (13) becomes

$$\frac{d}{dz}\left\{f[\eta_0]\frac{dc_0}{dz}\right\} = \alpha^2\eta_0 c_0$$

since η_0, the square root of the initial void fraction, is constant in z. After rearrangement, this becomes

$$\frac{d^2 c_0}{dz^2} - \gamma_0^2 c_0 = 0$$

Subjecting this equation to the above boundary condition yields the desired result.   ∎

In our second Lemma we show that the void function, $\eta(0, t)$ can be determined explicitly at the inlet (*i.e.,* left-hand boundary) for all time. This is significant because when the void function is zero, at $z = 0$, no more fluid can enter the solid and hence, the process ends.

Lemma 2 *When $z = 0$, the square root of the void fraction is given by*

$$\eta(0, t) = \eta_0 - \frac{1}{2}\beta t$$

Proof

From equations (12) and (14) it follows that

$$\frac{d\eta(0, t)}{dt} = \frac{-\beta}{2}c(0, t) = \frac{-\beta}{2}$$

Integrating from 0 to t yields the desired result.   ∎

Since η is intrinsically positive, t cannot exceed $\frac{2\eta_0}{\beta}$. We define $t_\beta \equiv \frac{2\eta_0}{\beta}$ to be the terminal time. Specifically, when $t = t_\beta$, the void η^2 is zero and no more gas can enter the pore.

Assumption

There exists a unique, positive, C^2 solution $\eta(z, t)$, of equations $(12) - (16)$ for all $(z, t) \in [0, 1] \times [0, t_\beta)$. It follows that there exists a C^2 solution, $c(z, t)$, on the same rectangle. Lemma 2.3 investigates the behavior of the concentration function. Here we show that the concentration is a positive function that decreases with z.

Lemma 3 *If*

$$\frac{\partial}{\partial z}\left\{f[\eta(z, t)]\frac{\partial c(z, t)}{\partial z}\right\} = \alpha^2 \eta(z, t)c(z, t) \quad (13)$$

and $c(0, t) = 1$ then

$$c(z, t) > 0 \text{ and } \frac{\partial c(z, t)}{\partial z} < 0 \,\forall (z, t) \in [0, 1] \times [0, t_\beta]$$

This follows from equation (13) and that $\eta(z, t_0)$, $f[\eta(z, t_0)]$ and A are positive.

Lemma 4 *$\eta(z, t)$ is an increasing function of z. Moreover,*

$$\eta(0, t) \le \eta(z, t) < \eta_0$$

Proof

From equation (2.0.1) it follows that

$$\eta(z,t) = \eta_0 - \frac{\beta}{2} \int_0^t c(z,\tau) d\tau$$

Since $c(z,t)$ is monotonically decreasing in z, $\eta(z,t)$ is monotonically increasing in z. The upper bound is a consequence of the non-negativity of β and c. ∎

Lemma 2.5 provides an upper bound for the concentration as a function of space. It shows that for each point z, the initial concentration is an upper bound for the concentration at that point.

Lemma 5 *If $c(z,t)$ satisfies (2.1), (2.2), $\frac{\partial c}{\partial z} < 0$ and*

$$c(z,0) = \frac{\gamma_0 \cosh \gamma_0 (1-z) + A \sinh \gamma_0 (1-z)}{\gamma_0 \cosh \gamma_0 + A \sinh \gamma_0}$$

where $\gamma_0 = \gamma(z,0) = \gamma(0,0) = \frac{\eta_0}{f(\eta_0)} \alpha$ then

$$c(z,t) \le c(z,0)$$

The proof is long and is omited for brevity.

Lemma 6 *From Lemmas 2.2, 2.4 and 2.5 it follows that*

$$
\begin{aligned}
\eta(z,t) &= \eta_0 - \frac{\beta}{2} \int_0^t c(z,\tau) d\tau \\
&\ge \eta_0 - \frac{\beta}{2} \int_0^t c(z,0) d\tau \\
&= \eta_0 - \frac{\beta}{2} c(z,0)t \ge \eta_0 - \frac{\beta}{2} c(z,0) t_\beta \\
&= \eta_0 [1 - c(z,0)]
\end{aligned}
$$

These inequalities provide lower bounds for the void fraction.

In summary

$\eta(z,t)$ decreases with time and increases with space. Moreover,

$$
\begin{aligned}
\eta_0 &\ge \eta(z,t) = \eta_0 - \frac{\beta}{2} \int_0^t c(z,\tau) d\tau \\
&\ge \eta_0 - \frac{\beta}{2} \int_0^t c(z,0) d\tau = \eta_0 - \frac{\beta}{2} c(z,0)t \\
&\ge \eta_0 - \frac{\beta}{2} c(z,0) t_\beta = \eta_0 [1 - c(z,0)].
\end{aligned}
$$

Since the void function is intrinsically positive, decreases with time, and

$$\eta(0,t) = \eta_0 - \frac{1}{2} \beta t$$

the process cannot proceed after time $t_\beta \equiv \frac{2\eta}{\beta}$ because the void at the inlet is zero.

The concentration decreases with z. Moreover,

$$c(1,t) \le c(z,t) \le c(z,0)$$

3.2 Successful Process

We will consider a definition of a successful process. In CVI, it is usually desirable to fill the porous solid as completely as possible before the time t_β. The solid is almost completely filled if the sum of the void fraction over space is small.

To investigate the completeness of the process, we define the average value of the void fraction

$$\bar{\epsilon}(t) \equiv \int_0^1 \eta^2(z,t) dz$$

The process will be $L_2 - successful$ if $\bar{\epsilon}(t)$ is less than some tolerance before the time t_β.

Let us clarify the difference between the final time t_f and the time t_β. For L_2-success, the time t_f, is the time that you assume the solid is filled within a given tolerance, that is, you think the void in the solid is as small as you want it to be, and you elect to stop the process. The time t_β, is the time when the void at the inlet is zero so fluid can no longer enter the solid. For a successful process $t_f < t_\beta$. For the successful numerical trials that we ran, t_f was more than 90% of t_β.

In the following section we will estimate the $L_2 - success$ of the process as the values α and A vary. First, we will get an upper bound on $\bar{\epsilon}(t_\beta)$.

3.3 L_2-success

Lemmas 2.7-2.11 and Theorem 2.1 describe the properties $\bar{\epsilon}(t)$.

An expression for the average value of the void fraction and that it is decreasing with time is the content of

Lemma 7 *If $\bar{\epsilon}(t) \equiv \int_0^1 \eta^2(x,t) dx$ then*

$$\frac{d\bar{\epsilon}}{dt} = \frac{\beta}{\alpha^2} \left\{ f[\eta(0,t)] \frac{\partial c(0,t)}{\partial z} + A f[\eta(1,t)] c(1,t) \right\}$$

and $\bar{\epsilon}(t)$ is decreasing with time.

Proof

$$
\begin{aligned}
\frac{d\bar{\epsilon}}{dt} &= \frac{d}{dt}\int_0^1 \eta^2(x,t)dx \\
&= 2\int_0^1 \eta(x,t)\frac{\partial\eta(x,t)}{\partial t}dx \\
&= -\beta\int_0^1 \eta(x,t)c(x,t)dx \\
&\qquad\qquad (2.3.1) \\
&= -\frac{\beta}{\alpha^2}\int_0^1 \frac{\partial}{\partial x}\left\{f[\eta(x,t)]\frac{\partial c(x,t)}{\partial z}\right\}dx \\
&= -\frac{\beta}{\alpha^2}\left\{f[\eta(1,t)]\frac{\partial c(1,t)}{\partial z} - f[\eta(0,t)]\frac{\partial c(0,t)}{\partial z}\right\}
\end{aligned}
$$

The third and fourth equalities follow from equations (12) and (13) respectively.

Noting that

$$\frac{\partial c}{\partial z}(1,t) = -Ac(1,t)$$

yields the desired equality.

That $\bar{\epsilon}(t)$ is decreasing follows from equation (2.3.1) and the fact that β, η and c are all positive. ∎

Lemma 2.8 provides an upper bound for the average value of void fraction as a function of time.

Lemma 8

$$
\begin{aligned}
\bar{\epsilon}(t) \leq \bar{\epsilon}_0 &- \frac{\beta}{\alpha}\int_0^t \left(\sqrt{\eta(0,\tau)f[\eta(0,\tau)]}\right. \\
&\left. \frac{\gamma_1\sinh\gamma_1 + A\cosh\gamma_1}{\gamma_1\cosh\gamma_1 + A\sinh\gamma_1}\right)d\tau \\
&+ \frac{\beta}{\alpha^2}A\int_0^t f[\eta(1,\tau)]c(1,\tau)d\tau
\end{aligned}
$$

Where $\gamma_1 = \gamma(0,t) = \sqrt{\frac{\eta(0,t)}{f[\eta(0,t)]}}\,\alpha$

The proof is omited for brevity.

Lemmas 2.9 and 2.10 prove inequalities that are useful in the proof of Theorem 2.1.

Lemma 9

$$\bar{\epsilon}_0 - \frac{\beta}{\alpha}\int_0^{t_\beta}\sqrt{\eta(0,\tau)f[\eta(0,\tau)]}\tan\gamma_1 d\tau \to 0$$

as $\alpha \to 0$

(Note that if A=0 then

$$\bar{\epsilon}(t_\beta) = \bar{\epsilon}_0 - \frac{\beta}{\alpha}\int_0^{t_\beta}\sqrt{\eta(0,\tau)f[\eta(0,\tau)]}\tan\gamma_1 d\tau$$

so $\bar{\epsilon}(t_\beta) \to 0$ as $\alpha \to 0$)

Lemma 10 *If $\gamma_1 < 1$ then*

$$\frac{1}{A+1}\frac{\gamma_1\sinh\gamma_1 + A\cosh\gamma_1}{\gamma_1\cosh\gamma_1} \leq \frac{\gamma_1\sinh\gamma_1 + A\cosh\gamma_1}{\gamma_1\cosh\gamma_1 + A\sinh\gamma_1}$$

Lemma 11 *We assert that if $z, A \in [0,1]$ then, for small values of γ_0, the initial concentration $c(z,0)$ has a maximum at $\gamma_0 = 0$.*

Theorem 12 *The void fraction is bounded below by*

$$\frac{1}{3}\left(\frac{A}{1+A}\right)^2 \epsilon_0$$

In Lemma 2.6 we showed that:

$$\eta(z,t) \geq \eta_0[1 - c(z,0)]$$

It follows that

$$\bar{\epsilon}(t) \equiv \int_0^1 \eta^2(z,t)dz \geq \int_0^1 \eta_0^2[1 - c(z,0)]^2 dz$$

$$(2.1.6)$$

Substituting $c(z,0)$ from equation (2.1.5) and integrating gives:

$$
\begin{aligned}
\bar{\epsilon}(t) \geq \eta_0^2 &\left[1 - \frac{2}{\gamma_0}\frac{A\cosh\gamma_0 + \gamma_0\sinh\gamma_0 - A}{\gamma_0\cosh\gamma_0 + A\sinh\gamma_0} + \right. \\
&\left. \frac{(\gamma_0^2 + A^2)\sinh 2\gamma_0 + 2\gamma_0(\gamma_0^2 - A^2) - 2a\gamma_0(1 - \cosh 2\gamma_0)}{4\gamma_0(\gamma_0\cosh\gamma_0 + A\sinh\gamma_0)^2}\right]
\end{aligned}
$$

It follows that $\bar{\epsilon}(t)$ is bounded from below as a function of $\gamma_0 = \gamma_0(\alpha_0)$, if A is fixed and $A > 0$. $\alpha \equiv$ (reaction rate)/(diffusion rate). Intuitively, if the diffusion rate increases and the reaction rate decreases a thin uniform coating of reactant will be deposited in the pores of the preform. Thus, as the ratio of the diffusion rate to the reaction rate decreases the final void fraction decreases. Rigorously, since $0 \leq c(z,0) \leq 1$, and $c(z,0)$ has a maximum at $\gamma_0 = 0$, $[1 - c(z,0)]$ has a minimum at $\gamma_0 = 0$.

Again, as $\alpha_0 \to 0$, $\bar{\epsilon}(t)$ goes to a minimum. Since $\gamma_0 \to 0$ as $\alpha \to 0$ we will take the limit as γ_0 goes to zero to find a lower bound for $\bar{\epsilon}(t)$.

From equation 2.1.5 and the Monotone Convergence Theorem it follows that

$$\lim_{\alpha_0 \to 0} \bar{\epsilon}(t) = \lim_{\gamma_0 \to 0} \int_0^1 \eta_0^2 [1 - c(z,0)]^2 dz$$
$$\geq \int_0^1 \eta_0^2 [1 - \lim_{\gamma_0 \to 0} c(z,0)]^2 dz$$

From equation 2.1.5 and L'Hopital's Rule it follows that

$$\lim_{\gamma_0 \to 0} c(z,0) = 1 - \frac{A}{1-A} z$$

Thus, the void fraction has the following lower bound

$$\bar{\epsilon}(t) \geq \frac{1}{3} \left(\frac{A}{1+A} \eta_0 \right)^2 = \frac{1}{3} \left(\frac{A}{1+A} \right)^2 \epsilon_0$$

Note that the lower bound for the void fraction increases with A. That is, increasing the flux of the reactant across the right-hand boundary (opposite the inlet) decreases the amount of pore filling that is possible.

The inequality of Theorem 2.1 tells us that the more uniform the flow, *i.e.* the less η and c vary with space, the smaller $\bar{\epsilon}(t_\beta)$ is. It provides an upper bound for the void fraction for small values of α.

Theorem 13 *If $\bar{\epsilon}(t) \equiv \int_0^1 \eta^2(z,t)dz$ and A is proportional to α^2 then*

$$\lim_{\alpha \to 0} \bar{\epsilon}(t_\beta) \leq A_0 \beta \int_0^{t_\beta} \{f[\eta(1,t)]c(1,t)$$
$$- f[\eta(0,t)]c(0,t)\} dt$$

where $A = A_0 \alpha^2$.

Proof

From Lemmas 2.8 and 2.10 it follows that

$$\bar{\epsilon}(t) \leq \bar{\epsilon}_0 - \frac{\beta}{\alpha} \int_0^t \left(\sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \times \right.$$
$$\left. \frac{\gamma_1 \sinh \gamma_1 + A \cosh \gamma_1}{\gamma_1 \cosh \gamma_1 + A \sinh \gamma_1} \right) dt$$
$$+ \frac{\beta}{\alpha^2} A \int_0^t f[\eta(1,\tau)]c(1,\tau)d\tau$$

$$\leq \bar{\epsilon}_0 - \frac{\beta}{\alpha} \int_0^t \left(\sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \frac{1}{A+1} \times \right.$$
$$\left. \frac{\gamma_1 \sinh \gamma_1 + A \cosh \gamma_1}{\gamma_1 \cosh \gamma_1} \right) d\tau$$

$$+ \frac{\beta}{\alpha^2} A \int_0^t f[\eta(1,\tau)]c(1,\tau)d\tau$$

$$\leq \bar{\epsilon}_0 - \frac{\beta}{\alpha} \frac{1}{A+1} \int_0^t \sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \tan \gamma_1 d\tau$$
$$- \frac{\beta}{\alpha} \frac{A}{A+1} \int_0^t \frac{1}{\gamma_1} \sqrt{\eta(0,\tau)f[0,\tau]} d\tau$$
$$+ \frac{\beta}{\alpha^2} A \int_0^t f[\eta(1,\tau)]c(1,\tau)d\tau$$

Noting that $\frac{1}{A+1} \approx 1 - A$, $\gamma_1 = \sqrt{\frac{\eta(0,t)}{f[\eta(0,t)]}} \alpha$ and $c(0,t) = 1$ tells us that

$$-\frac{\beta}{\alpha} \frac{1}{A+1} \int_0^t \gamma_1 \sqrt{c(0,\tau)f[\eta(0,\tau)]} d\tau \approx$$
$$-A \frac{\beta}{\alpha^2} \int_0^t f[\eta(0,\tau)]c(0,\tau)d\tau$$
$$+A^2 \frac{\beta}{\alpha^2} \int_0^t f[\eta(0,\tau)]c(0,\tau)d\tau$$

and

$$\frac{\beta}{\alpha} \frac{1}{A+1} \sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \tan \gamma_1 d\tau \approx$$
$$\frac{\beta}{\alpha} \int_0^t \sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \tan \gamma_1 d\tau$$
$$-A^2 \frac{\beta}{\alpha^2} \int_0^t \sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \tan \gamma_1 d\tau$$

Thus,

$$\bar{\epsilon}(t) \leq \bar{\epsilon}_0 - \frac{\beta}{\alpha} \int_0^t \sqrt{\eta(0,\tau)f[\eta(0,\tau)]} \tan \gamma_1 d\tau$$

$$+A_0\beta \int_0^t \{f[\eta(1,\tau)]c(1,\tau) - f[\eta(0,\tau)]c(0,\tau)\} d\tau$$

$$+A_0^2 \alpha^2 \beta \int_0^t \left\{ f[\eta(0,\tau)]c(0,\tau) - \sqrt{\eta(0,\tau)} \tan \gamma_1 \right\} d\tau$$

The conclusion follows from Lemma 2.9.

$$QED$$

We conclude this section with some interpretations of the last estimate. Recall that

$$f[\eta(1,t)] \leq f(\eta_0)$$

$$\eta(0,t) = \eta_0 - \frac{\beta}{2} t$$

$$c(1,t) \leq c(z,t)$$

$$c(z,t) \leq c(z,0)$$

$$c(0,t) \equiv 1$$

From equation 2.3.3 it follows that

$$\bar{\epsilon}(t) \leq \bar{\epsilon}_0 \quad - \quad \frac{\beta}{\alpha}\int_0^t \sqrt{\eta(0,\tau)f[\eta(0,\tau)]}\tan\gamma_1 d\tau$$
$$+A\frac{\beta}{\alpha^2}\int_0^t \{f(\eta_0)c(1,0) - f[\eta(0,\tau)]\}\,d\tau$$
$$+ \quad A^2\alpha^2\int_0^t \{f[\eta(0,\tau)]c(0,\tau)-$$
$$\sqrt{\eta(0,\tau)}\tan\gamma_1\Big\}\,d\tau \qquad (2.3.4)$$

Note that every term on the RHS of equation (2.3.4) is known or measurable. So, if you know how long you want to run the process you can compute a sharp upper bound on $\bar{\epsilon}$. Or, if you know the desired void fraction, the time, and the relation between α and β you can use (2.3.4) to attain an upper bound for α.

Finally, as $\alpha \to 0$ and $t = t_\beta$

$$\bar{\epsilon}(t_\beta) \leq A_0\beta\left\{f(\eta_0)c(1,0)t_\beta - \int_0^{t_\beta} f\left[\eta_0 - \frac{\beta}{2}t\right]dt\right\}$$
$$(2.3.5)$$
$$= 2A_0\eta_0\left\{f(\eta_0)c(1,0) - A_0\beta\int_0^{t_\beta} f\left[\eta_0 - \frac{\beta}{2}t\right]dt\right\}$$

4   Conclusion

Recall that α and β can be determined from the initial conditions, reaction rates, diffusion rates, and molar volume (c.f. 1.2.16). The void at the inlet is a function of β and time (c.f. Lemma 2.2) γ_1 is a function of the void at the inlet times α (c.f. Lemma2.8) Finally, A can be determined from the ratio of the concentration gradient to the concentration and $f(\eta) = \frac{1}{3}\frac{\rho\eta^3}{\rho\eta + 1.5410^{-5T}}$. Thus, using Theorem 2.1, the maximum amount of pore filling can be determined.

An upper bound for the void fraction as a function of time can be calculated using equation 2.3.4. Note that if the reaction rate is very small compared to the diffusion rate then the deposition is of solid is uniform along the axis of the pore. Under these ideal conditions ($\lim_{\alpha_0 \to 0} \bar{\epsilon}(t)$) one can use the afore mentioned equation to calculate an upper bound for the void.

When the inlet is closed and all subsequent mass gain is on the surface of the material (c.f. Lemma 2.2).

Thus, these estimates can be used to adjust parameters and determine the outcome of experiments for the production of CVI composites.

[†] This formulation is a modification of the formulation given in the first reference.

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