**GAS TRANSPORT MODEL FOR
CHEMICAL VAPOR INFILTRATION**

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May 1995

Report prepared by
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ABSTRACT

A node-bond percolation model is presented for the gas permeability and pore surface area of the coarse porosity in woven fiber structures during densification by chemical vapor infiltration (CVI). Model parameters include the number of nodes per unit volume and their spatial distribution, and the node and bond radii and their variability. These parameters relate directly to structural features of the weave. Some uncertainty exists in the proper partition of the porosity between "node" and "bond" and between intra-tow and inter-tow, although the total is constrained by the known fiber loading in the structure. Applied to cloth layup preforms the model gives good agreement with the limited number of available measurements.

INTRODUCTION

For forced flow chemical vapor infiltration (CVI) the gas permeability of the preform and the partially dense composite is a critical factor in the success of the process. The gas permeability of the material controls the pattern of reactant flow through the preform and sets the limit for the ultimate achievable density. Previous efforts to estimate gas transport properties and their evolution during CVI densification have been limited. It is important to note that estimation of the initial properties of the preform is not sufficient for this application. The transport properties of the material change as density increases and a suitable model must track this change. In particular, the limiting behavior near full density is very important as this determines to a great extent the final microstructure of the composite.

Early work by Naslain and co-workers^{1,2} modeled the preform as a collection of cylindrical, monosized pores and estimated the effective diffusion coefficient for the material as the pores filled during CVI. Convective flow of gas was not considered although this simple microstructure would allow a relatively straightforward extension of the model to include gas permeability. This simple microstructure, however, is not a good representation of real woven preforms and cannot provide quantitative estimates of transport properties.

For randomly oriented, short fiber preforms Starr³ proposed a structure model based on an orthogonal array of cylinders and used this model to estimate surface area and gas permeability during CVI. This microstructure model is more realistic in that it includes a distribution of pore

sizes. Developed for chopped fiber preforms the model does not represent anisotropic woven materials.

Yu and Sotirchos⁴ proposed a generalized pore model for gas-solid reactions based on an interconnected network of cylindrical pores with a distribution of diameters. Percolation theory is used to predict creation of trapped porosity as density increases and the smaller pores are filled. This feature is an important advance since residual, inaccessible porosity is always present in "fully" infiltrated CVI processed composites. This approach has been tested using Monte Carlo simulation⁵ and applied to CVI processing^{6,7,8,9,10}. While this approach has many desirable features, the structure model employed does not relate well to the anisotropic, woven fiber structures commonly used for CVI preforms.

For cloth layup preforms Starr¹¹ used a semi-empirical approach relating the anisotropic gas permeability and diffusion coefficient to the contrasting properties of the cloth-containing regions and the regions between cloth layers. While introducing anisotropy as a model feature, this approach does not relate properties directly to microstructure but relies on experimental measurements to provide model parameters.

Also for woven cloth preforms, Chung et al.^{12,13} employed a model that explicitly includes such structural features as tow and cloth spacing and the number and size of filaments in the tows. This model includes diffusional transport only and cannot be used to estimate gas permeability. Also, this model does not include percolation effects and the creation of inaccessible porosity.

MODEL DESCRIPTION

A general model for the microstructure and gas permeability of woven fiber preforms and composites is based on a node-bond model. In this model the porosity is represented as a network of spherical "nodes" connected by cylindrical "bonds" (Figure 1). The network geometry is directly related to the regular structure of the woven preform. Nodes correspond to the large pores created at tow crossing points while bonds correspond to the smaller channels that connect neighboring nodes. The spatial arrangement of the nodes and their coordination number (number of nearest neighbors) is fixed by the weave architecture i.e. tow spacing and weave or braid pattern. Values of the node and bond diameters exhibit a distribution of values around an average which is set to match the overall volume fraction of intertow porosity.

The gas permeability of this network is calculated assuming Poiseuille flow through the cylindrical bonds with the given distribution of diameters. Densification is simulated by incrementally reducing the bond and node dimensions and recalculating the network pore volume, surface area and permeability. As densification proceeds the smaller bonds close (Figure 2) and as the fraction of open bonds approaches the percolation limit the accessible pore fraction and the network permeability both vanish exponentially.

Uniform Pore Structure

Consider that the porous body contains a number of nodes (or sites), N , per unit volume and that these are connected by gN bonds (coordination number of $2g$). Assuming spherical nodes and cylindrical bonds, the volume V and surface area S of this network of pores, per unit volume, are:

$$V = N \left(\frac{4}{3} \pi R_n^3 + g \pi H R_b^2 \right)$$

$$S = N (4 \pi R_n^2 + 2 g \pi H R_b)$$

where R_n is the radius of the node and R_b and H are the radius and length of the bonds.

The Darcy permeability in the z -direction, k_z , of this network is calculated assuming Poiseuille flow through the bonds. The pressure drop, Δp , through a cylinder with volumetric flow, q , is:

$$\Delta p = \frac{8 \mu H}{\pi R_b^4} q$$

for a fluid with viscosity μ . For our unit volume the pressure drop across two opposing faces, ΔP , is:

$$\Delta P = N_z \Delta p$$

where N_z is the number of sequential channels through which the flow passes between two faces of the unit volume.

Figure 1. Node-bond model represents the structure of the coarse porosity in a woven fiber preform. Gas transport through the preform is represented by viscous flow through this network.

Figure 2. During CVI densification the smaller bonds close first. Transport continues until the fraction of open bonds reaches the percolation limit.

The total flow, Q , through these faces is:

$$Q = \frac{gN}{N_z} q$$

giving the overall pressure/flow relationship as

$$\Delta P = \left(\frac{8HN_z^2}{\pi gNR_b^4} \right) \mu Q = \frac{1}{k_z} \mu Q$$

The permeabilities in the x- and y-directions depend similarly on the values N_x and N_y .

In the chemical vapor infiltration (CVI) process the porosity of the composite preform is reduced by deposition of solid matrix material onto the internal surface area. For a given deposit thickness, C , the pore volume, surface area and permeability become:

$$V = N \left(\frac{4}{3} \pi (R_n - C)^3 + g \pi H (R_b - C)^2 \right)$$

$$S = N (4 \pi (R_n - C)^2 + 2 g \pi H (R_b - C))$$

$$k_z = \frac{\pi g N (R_b - C)^4}{8 H N_z^2}$$

These quantities depend only on the microstructure features of pore size (R_n and R_b) and spacing (N_x , N_y , N_z). (The value of H can be calculated from the values of these parameters.)

Dimensional relationships of V , S and k_z are more apparent when the above three equations are rearranged using the definitions:

$$L = N^{-1/3} \quad L_z = 1/N_z$$

and redefining the node and bond dimensions as relative values,

$$r_n = \frac{R_n}{L} \quad r_b = \frac{R_b}{L} \quad h = \frac{H}{L} \quad c = \frac{C}{L}$$

This gives

$$V = \frac{4}{3}\pi(r_n - c)^3 + g\pi h(r_b - c)^2$$

$$S = \frac{1}{L} (4\pi(r_n - c)^2 + 2g\pi h(r_b - c))$$

$$k_z = L_z^2 \frac{\pi g(r_b - c)^4}{8h}$$

The relative pore volume depends only on dimensionless quantities, as expected, while the surface area and permeability depend on the absolute values of the microstructure dimensions. For a given fraction porosity the surface area increases inversely with pore size and the permeability increases with increasing spacing in the flow direction. For anisotropic structures the permeability will be anisotropic depending on the square of the ratio of the spacings in orthogonal directions.

Non-uniform Pore Structure

The pore model described above clearly is not realistic in that it assumes single values for all of the structure parameters describing the pore network. In a real porous network the pores have a range of sizes generally about one or more modal values. Considering this we replace the appropriate terms in the above equations with the averaged values: $\langle (r_n - c)^3 \rangle$, $\langle h(r_b - c)^2 \rangle$, $\langle (r_n - c)^2 \rangle$, $\langle h(r_b - c) \rangle$, and $\langle (r_b - c)^4/h \rangle$ where the averaging process includes only those terms with r_n and $r_b > c$. For relatively simple size distributions, this averaging may be accomplished analytically, however, numerical methods usually will be required.

Percolation Limit

With a range of initial pore sizes and a given value of deposit thickness, c , some pores are completely filled while others remain open. Percolation theory¹⁴ recognizes that no connected path exists after a certain fraction of bonds are closed. The remaining porosity is isolated and does not contribute to the available surface area or to fluid flow. The percolation

limit for a conducting network depends on its dimensionality and connectivity. Thus, regular 3-dimensional networks with cubic, body-centered cubic (BCC) and face-centered cubic (FCC) connectivity will no longer conduct when less than 31.16%, 24.6% and 19.8% of the bonds are open.

As the network approaches the percolation limit, isolated clusters of pores are formed. These do not contribute to the available surface area or to the overall conductivity of the network. The fraction of bonds that are connected to the "volume spanning cluster" (the "strength" of the network) and the conductivity of this cluster each approaches zero as the network approaches the percolation limit. This approach has an exponential dependence. For 3-D networks the exponent values for network strength and conductivity are 0.41 and 2.0 respectively.

PARAMETRIC DEPENDENCE OF PERMEABILITY AND SURFACE AREA

The parametric dependence of permeability and surface area can be understood by examining the non-dimensional groups SL and k/L^2 . These depend on the mean values of r_n and r_b , and on the widths of their distributions. This will be shown with a body-centered cubic pore structure with eight channels connecting each pore to its nearest neighbors ($n=4$), and assuming that the pore sizes follow a ln-normal distribution:

$$P(r) = \frac{r_0}{\sqrt{2\pi} \sigma} \frac{\exp\left(-(\ln r - \ln r_0)^2 \frac{r_0^2}{2\sigma^2}\right)}{r}$$

where r_0 and σ are the median and width of the distribution.

Figures 3-5 below show the change in the permeability as the pores close during CVI for three parameters: the starting porosity prior infiltration, the ratio of the node and bond radii, and the widths of the node and bond radius distributions as a percentage of the median value. Figure 3a plots dimensionless permeability for starting porosities 10, 20 and 30% with fixed node/bond ratio and distribution. The initial permeability increases with increasing porosity, however, at intermediate porosity the higher initial porosity preform has lower permeability. The initial surface area also is higher for greater starting porosity but is lower near the end of densification. As seen in both figures, the amount of trapped porosity at the end of the process increases with increasing starting porosity.

Figures 3. The dimensionless permeability (a) and surface area (b) are plotted for starting porosities 10, 20 and 30% with fixed node/bond ratio of 3.0 and distribution width of 20%.

Figures 4. The dimensionless permeability (a) and surface area (b) are plotted for node/bond ratios of 1.0, 2.0 and 3.0 with starting porosity of 20% and distribution width of 20%.

Figures 5. The dimensionless permeability (a) and surface area (b) are plotted for distribution widths of 10, 20 and 30% and with node/bond ratio of 3.0 and starting porosity 20%.

Figure 4 shows the permeability and surface area for a starting porosity of 20% and a radius distribution width that is 20% of the median value. As the bonds get smaller relative to the nodes the permeability decreases. The initial surface area is very similar for the different node/bond ratios, but the amount of trapped porosity increases as this ratio increases.

Figure 5 shows the permeability and surface area for a starting porosity of 20% and an node/bond ratio of 3.0 for different distribution widths. As the variability in pore size increases, the initial permeability increases. This trend reverses at higher density as the more variable structure produces a greater amount of trapped porosity. The surface area is smaller at all densities for the more variable pore structure.

Overall, for a given amount of porosity in the preform, increased uniformity of the pore structure leads to increased permeability, higher surface area and reduced trapped porosity.

MODEL CALCULATION FOR WOVEN FIBER PREFORM

The model can be used to estimate the surface area and permeability of woven fiber preforms during CVI. A commonly used preform consists of several layers of square-weave cloth stacked with or without rotation between layers and compressed to give 40% fiber by volume. A typical preform uses tows of 15 μm fibers with 500 filaments/tow, tow spacing of 0.150 cm in the cloth (X and Y directions) and a layer spacing of 0.030 cm. These parameters yield an overall fiber loading of 40%. The 60% porosity is divided approximately equally between fine porosity within the tows and coarse porosity between the tows. The coarse porosity consists of relatively large pores (nodes) in the plane of the cloth and smaller, tortuous pores connecting these to eight similar nodes in adjoining cloth layers.

This preform structure yields values of L , L_z and L_x of 0.0877, 0.0300 and 0.0750 cm respectively. The gas permeability is calculated using the node-bond model described above assuming $r_n/r_b = 3.0$, a starting pore volume of 30% and a log-normal pore size distribution with a width of 20% of the median value. This estimate is shown in Figure 6 for flow parallel and perpendicular to the cloth. The ordinate values in Figure 6 are adjusted to include the fine porosity within the tows which is estimated to be 30% initially and 7% (90% solid volume within the tow) after 0.0005 cm has been deposited. This adjustment allows comparison with experimental values which are reported relative to the overall fractional density of the

composite¹¹. The agreement between model and experiment is good and could be improved by adjusting the model parameters.

Surface area per unit volume of the open inter-tow porosity is plotted in Figure 7 and compared to experimental measurements using high resolution X-ray tomography¹⁵. These measurements include surface area associated with closed porosity although this is likely to be small over the range of density studied. The agreement between model and experiment is good; the model values are somewhat lower than experiment for the initial preform.

DISCUSSION AND CONCLUSIONS

The node-bond percolation model for gas transport builds on a representation of the coarse porosity in woven fiber structures during CVI densification. While this structure is idealized, model parameters relate to real structural features such as filament size, number of fibers per tow and spacing of tows in the weave. Some uncertainty exists in the proper partition of the porosity between "node" and "bond" and between intra-tow and inter-tow, although the total is constrained by the known fiber loading in the structure. The variation of the structure also influences the predicted gas permeability, particularly near full density.

Applied to cloth layup preforms the model gives good agreement with the limited number of available measurements. Extension to other fiber architectures is straightforward, however, no experimental results are available for comparison.

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Figure 6. Calculated and experimental gas permeability for cloth layup preform during CVI densification.

Figure 7. Calculated and experimental surface area for cloth layup preform during CVI densification.