

Chemical Vapor Infiltration of Thin Carbon Bodies

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Introduction

SGL Carbon Composites manufactures a single ply composite material for use in wet friction applications. To make this material, woven carbon fiber fabric is densified to a targeted percentage mass gain and a targeted crust thickness using chemical vapor infiltration (CVI) of carbon from natural gas. The infiltration model presented here was generated to understand the main factors that influence the mass gain and crust thickness.

Since the fabric material is thin, the model assumes a uniform growth rate in all areas of the fiber tow. For growth within the fabric, the model tracks the fiber coating thickness, accounting for the increase in surface area as bare fibers thicken, and reduction of surface area which occurs when fibers begin to "grow" together. Additional mass gain is then only due to continued growth of the tow outer surface "crust".

The possibility of pore closing before full infiltration is handled in an average way by setting a limit to the minimum local porosity attainable. A small or zero value for this limit indicates no diffusion barrier at any time in the process. A higher value models the rapid filling of near surface porosity to leave high levels of closed porosity inside the fiber tow.

Hexagonal Model Geometry

For circular fibers, the most compact arrangement of fibers is hexagonal close packed, giving a maximum of about 90% fiber volume, or 10% porosity.

Because the tow is subjected to handling processes, the fiber volume percent is more typically in the 60-70% range. Some fiber tows are intentionally disrupted (as in stretch broken yarns), giving a much smaller effective fiber volume percent (20-40%). The weaving parameters of the cloth also affect this value, with looser, lower pic count weaves resulting in lower fiber volume fractions.

The local fiber volume fraction ranges over values significantly higher and lower than the total average. This random type of arrangement in modeled by assuming local regions of the fiber tow can be characterized by hexagonal close packed arrangements, but with a distribution of unit cell sizes such that the net average fiber volume is correct.

This is illustrated in Figure 1, which shows representative areas of greater or lesser fiber volume fraction within a tow with a given average fiber volume fraction.

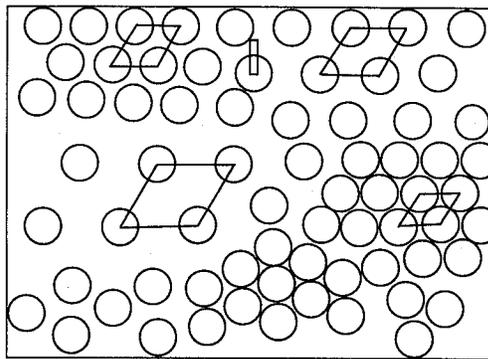


Figure 1. Fiber volume distribution can be modeled assuming a distribution of effective unit cell sizes.

Mass Gain Rate Calculation

Within a uniform fiber volume fraction region, the mass gain rate is determined by the deposition rate per unit surface area (a parameter in the model which depends on the processing conditions), times the surface area exposed to the gas. The surface area is calculated at any time during the process from the geometry of the unit cell and the growing front of the carbon coating being deposited.

The surface area/volume represents the heart of the model. It describes how the surface area changes during the densification process, and drives the main result for the percentage mass gain. The total fabric surface area per unit volume has two components, the outer fabric surface itself (A_{fab}) and the interior surface area (A_s) represented by pore walls within the tow.

$$A = A_{fab} + A_s$$

The tow surface area per unit volume calculation depends on whether the pyrocarbon thickness is below the critical thickness, between the critical thickness and the interior thickness limit, or greater than the interior thickness limit. Figure 2 shows the geometrical relationships appropriate for these regions.

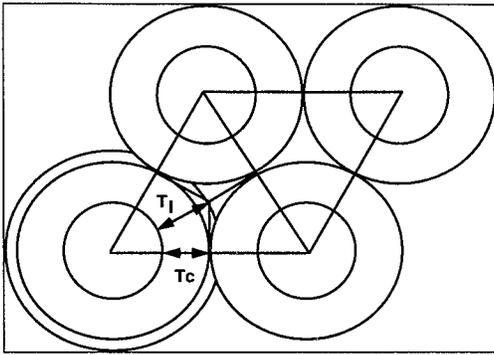


Figure 2. Geometric construction indicating the critical thickness for bridging, T_c , and the limiting thickness for deposition within the unit cell, T_l .

Below the critical thickness, the surface area per unit cell is represented by six arc segments of arc angle $\pi/3$ with an arc radius equal to the fiber radius plus the CVI thickness.

$$A_s = 6 \pi/3 (D/2 + T) / (S^2 \cos(\pi/6))$$

Where T is the deposited carbon thickness

Above critical thickness, the surface to volume is determined by the same formula as before, but now the arc angle (argument of the cos function) depends on the thickness of the CVI coating. The growing CVI joins with growth from adjacent fibers along a line starting at the midpoint between adjacent fibers and extending perpendicular from that line to the geometric center of a group of three fibers.

$$\text{Arc angle} = \pi/3 - 2 \cos^{-1}((D/2 + T_c) / (D/2 + T))$$

Once all interior surface area has been filled, the only surface area remaining is the external surface area of the fiber tow. This surface area is essentially constant from the beginning of densification, and contributes a constant area/volume for growth to occur. This area/volume value is provided as a variable in the model to account for variations in the fiber tow shape, and for the possibility that some additional surface area of large pores can contribute to this mass accumulation.

The above relations apply to local areas of the fabric which represent a fraction of the total fabric. Multiplying each such area by the fraction of the total volume in the fabric with that local fiber volume fraction, the contributions can be integrated to give the total average growth rate.

Experimental Comparisons

Figure 3 shows two densification curves obtained using a CVI reactor equipped with a mass balance to record the mass of the sample during densification. The two curves correspond to two different types of starting fabric. One is

a continuous fiber plane woven yarn, the other is a stretch broken fiber plane woven yarn. The two materials were processed at exactly the same processing conditions.

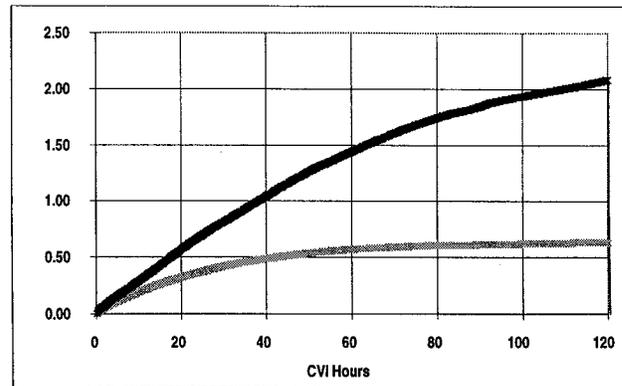


Figure 3. Densification curves of a stretch broken yarn fabric and a continuous fiber fabric under the same processing conditions.

The two samples start with the same weight gain rate, since the two fibers have the same diameter and same density. The continuous fiber fabric, however, rapidly shows indications of a reduction in surface area, with the interior tow volume showing complete filling within a few tens of hours. The stretch broken fabric, however, continues to increase in weight in a near linear fashion for a long period. (Some bridging has to be occurring early; otherwise, the densification rate would actually increase. The near linear behavior indicates that these two effects are in near balance).

Figure 4 shows simulated curves for the two materials, where the average fiber volume fraction and the fiber volume fraction distribution has been adjusted to conform the those measured for the two materials.

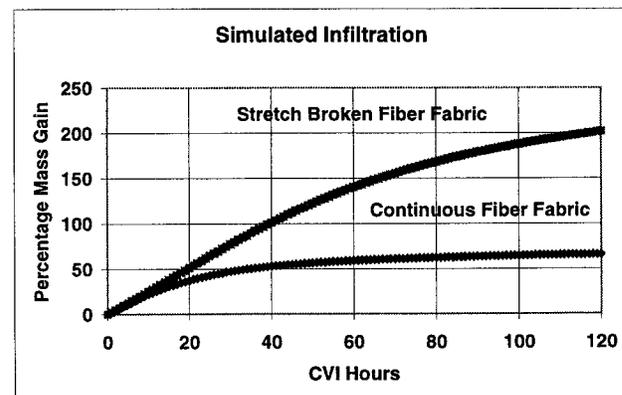


Figure 4. Calculation of Stretch Broken and Continuous Fiber Fabric infiltration

The simulations were run using a fiber volume fraction within the fiber tow of .75 for the continuous fiber fabric and 0.28 for the stretch broken fiber fabric. These values are very close to those calculated for the two materials.