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# Calculation of the evolution of surface area and free volume during the infiltration of fiber felts

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**Abstract**

For the chemical vapor infiltration of pyrolytic carbon the ratio of surface area to free volume plays a crucial role in understanding and modeling the deposition process. Here, the evolution of surface area and free volume during the infiltration of fiber felts was calculated quantitatively.

For parallel fibers in a square or hexagonal 2D lattice the evolution was calculated analytically using simple geometrical considerations. For this case one local minimum in the ratio of surface area to free volume vs. radius of the fibers was found.

For overlapping fibers the evolution was approximated using a Boolean model. For this model, the ratio of surface area to free volume was obtained analytically for fibers with any degree of orientation anisotropy. We find that the ratio of surface area to free volume increases linearly with the radius of the fibers. The model also allows to estimate surface area, free volume and surface area / free volume ratio for felts with non-overlapping fibers for low initial filling factors.

Finally, models of felts with randomly distributed, non-overlapping fibers with different degrees of orientation anisotropy, including parallel fibers and isotropic orientation of the fibers, were generated. Based on these models the evolution of surface area and free volume were calculated numerically. The surface area / free volume ratio increases nearly linearly for all initial filling factors and for all degrees of orientation anisotropy up to a filling factor of 95 %.

Our data allow the calculation of the evolution of A/V for typical infiltration experiments based only on the knowledge of the fiber felt parameters.

*Keywords:* Carbon Composites, Chemical Vapor Infiltration, Modeling, Surface Area

## 1. Introduction

The chemical vapor deposition of pyrolytic carbon as well as the chemical vapor infiltration of fiber felts with pyrolytic carbon is of great technological as well as scientific interest. Nevertheless the deposition process has not been understood in detail. Only in the recent years it has been commonly accepted that the maturation of the gas phase is not only influenced by the ‘classical’ parameters of chemical vapor deposition and infiltration like gas pressure, temperature and residence time but also strongly by the ratio of surface area A to free volume V. The interaction of homogeneous gas-phase and heterogeneous surface reactions is controlled by the A/V ratio: for small A/V homogeneous gas-phase reactions are favored. For high A/V heterogeneous surface reactions dominate.

In this paper [1] we present the first quantitative data for the evolution of A/V using analytical calculations for parallel fibers in a square or hexagonal 2D lattice and for felts with overlapping fibers and applying numerical simulations for felts consisting of non-overlapping fibers.

## 2. Analytical Calculation Based on a Boolean Model

In stochastic geometry, stationary random closed sets are used to describe macroscopically homogeneous but microscopically heterogeneous structures. The Boolean model is based on a stationary Poisson point process. To create a realization of a Boolean model, first the Poisson process is simulated. In our case, the fibers are long compared to the size of the observation window. That is, it is very unlikely to observe fiber ends in the sample. Therefore, a model based on a Poisson line process is appropriate. A Poisson line process is a Poisson point process on the space of one-dimensional affine subspaces of $\Re^3$. It is completely described by its intensity λ (the expected total line length per unit volume) and the distribution of the directions of lines. The line process is called isotropic if its distribution is invariant with respect to rotations. That is, the directions are uniformly distributed.

Dilating the line system using a ball yields a system of straight cylinders with circular cross sections. The union of these cylinders or fibers is a generalized Boolean model. Formulae for surface area A per free volume V in terms of the model parameters (intensity λ and radius of the cross section r) of the Boolean fiber model can be derived that are valid for the isotropic and for the anisotropic case [2]:

$$\frac{A}{V} = \lambda\, 2\pi\, r,$$

where A/V is a linear function of r.

## 3. Numerical Simulation

The analytical calculations above hold for the Boolean model, where fibers can be infinitely close, only. A more realistic model is obtained if the fibers are not allowed to

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intersect. The resulting, so-called hard core model can not be described analytically anymore. Therefore, simulations for different degrees of orientation anisotropy and different filling factors were carried out. Two steps were necessary: in the first step the fiber felts were randomly generated using the GeoDict software (Version 1.00, Fraunhofer Institute for Industrial Mathematics, Kaiserslautern, Germany).

Fig. 1. Realization of a random fiber system with isotropic orientation, filling factor 10 %.

Once a fiber felt structure had been generated (e.g. Fig. 1), in a second step the data was processed with a software package (a4iL, version 1.2.2, Fraunhofer Institute for Industrial Mathematics, Kaiserslautern, Germany). The Euclidean distance transform was carried out determining the distance of each voxel to the fiber structure. Based on this distance data, 3D images containing all voxels with a certain maximum distance from the fiber felt (corresponding to the thickness of the deposited layer) and the felt itself were generated. Then the surface area A and the free volume V were calculated. By increasing the maximum distance from the fiber felt, the evolution of A and V during the infiltration process could be modeled.

Fig. 2 shows exemplary results: V, A and A/V vs. layer thickness for an isotropic felt with an initial filling factor of 10 % are shown. The average data of numerical simulations is compared with the Boolean model. The Boolean model yields a slower decrease in free volume as well as a slower initial increase in surface area. For thicker layers, the surface area drops off slower for the Boolean model. A/V increases nearly linearly in the numerical simulation with a slope of 0.319 $R^{-2}$ as compared to a linear increase with a slope of 0.2 $R^{-2}$ for the Boolean model.

## 3. Conclusions

Surface area A, free volume V and A/V during the infiltration of fiber felts were calculated quantitatively for different degrees of anisotropy of the orientation of the fibers and different initial filling factors.

For parallel fibers in a 2D lattice the evolution was calculated analytically applying the four fiber model or the three fiber model, respectively (not discussed in this extended abstract). For this case a local maximum and a local minimum in the A/V vs. radius curve were found.

The evolution of A/V in felts with overlapping fibers can be calculated by the analytical Boolean model. Here, the ratio of surface area to free volume increases linearly with radius of the fibers. The model is suitable to estimate A, V and A/V also for felts with non-overlapping fibers for low initial filling factors.

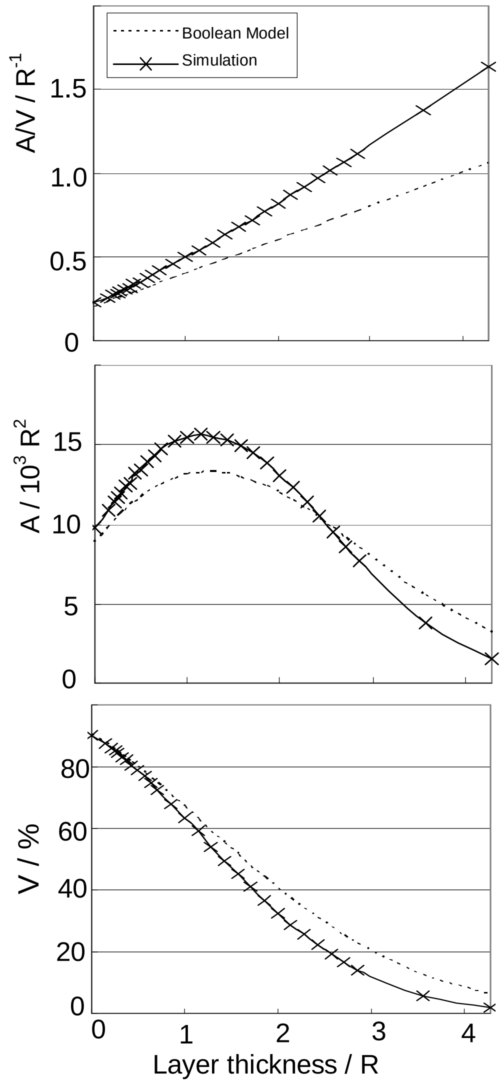


Fig. 2. Numerical calculation of free volume V, surface area A and A/V as a function of the radius of a fiber R for a felt with isotropic orientation consisting of randomly distributed fibers (initial filling factor 10 %) in comparison with the Boolean model. Note that A/V is proportional to the radius of the fibers in the Boolean model.

Finally, numerical simulations were carried out to be able to determine the evolution of A, V and A/V where analytical models were no longer suitable i.e. the fibers neither are parallel and arranged in a 2D lattice nor are allowed to intersect. No local minima in the ratio of surface area to free volume vs. radius were found. A/V increases nearly linearly for all initial filling factors and for anisotropy factors. The data on the evolution of A/V during the infiltration of fiber felts presented in this paper allow an estimation of the evolution of A/V for typical infiltration experiments only based on the knowledge of the fiber felt parameters.

## References


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