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## Process-based model of mixed-matrix membrane

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The microstructure of a composite material and the physical characteristics of its phases determine macroscopic (effective) properties of the medium. These properties together with physical and chemical characteristics of fluids being transported in the medium further define transport and equilibrium properties of engineering interest, such as permeability, diffusivity, and solubility. Relationships between the microstructure (a spatial distribution of the phases) and effective properties are therefore of great theoretical and practical interest in many fields of technology.

Approaches to microstructure reconstruction involve direct measurements available via X-ray computed microtomography, a number of statistical models of measuring statistical properties, such as porosity, correlation and lineal path functions on two-dimensional (2D) images of cuts through the sample, and process-based models. In contrast to statistical models, process-based models try to simulate the composite structure as a result of physical and chemical processes.

Mixed-matrix membranes contain various solid and/or liquid fillers embedded in a polymer matrix. For gas separation processes, mixed-matrix membranes made of a particulate solid and polyimide often reveal higher permeability and, simultaneously, equal or greater selectivity than conventional polyimide membranes, particularly at elevated temperatures. In recent experimental studies it was shown that complex interfaces between both phases have a significant effect on transport properties of the mixed-matrix membranes. However, a quantitative explanation of these empirical phenomena has not been given yet. Therefore, it is worth reproducing the membrane microstructure and relating it to the enhanced transport properties.

The focus of this contribution was on the formulation and verification of a process-based model of the mixed-matrix membrane that consisted of the polyimide matrix synthesized from the monomers 4,4'-(hexafluoroisopropylidene)diphtalic anhydride and 4,4'-oxydianiline, and silicalite-1. When a solution of a polyimide precursor in N,N-dimethylformamide was ready, silicalite-1 particles were dispersed in the solution and the dispersion was subsequently cast on a Teflon support plate. An initial mass ratio of silicalite-1 and polyimide was about 1:1. After solvent removal, the films were heated in subsequent steps up to 230°C for two hours (the precursor was transformed into polyimide). From a process-based model point of view, a key operation of the entire synthesis was slow sedimentation of silicalite particles in the viscous solution. Preliminary observation of 2D cuts through the solid membrane in a scanning electron microscope revealed that there were a lot of contacts among the silicalite particles. Therefore, a sequential (ballistic) deposition algorithm, well representing sedimentation in a low-energy environment, was used to create an off-lattice model of spatial distribution of the silicalite particles in the polyimide matrix.

It followed from back-scattered electron image analysis that most of the silicalite particles were well rounded. A particle size distribution was constructed, assuming approximately spherical shape, by numbering and sorting all particles according to size. Its

mean diameter was about 14 nm. A predefined number of spheres were sequentially settled in a cubic simulation box. Each sphere, the size of which was drawn at random from the particle size distribution, got an initial position. Its horizontal coordinates were picked at random from the uniform distribution, the domain of which was given by a box size. The initial vertical coordinate was derived from the maximum height of a deposited layer. Then the sphere fell under the action of its own weight in a gravitational field. It was assumed that its velocity quickly reached a steady value given by a force balance involving the Stokes law, the gravitational force and the buoyant force, i.e. the velocity was directly proportional to the squared diameter of a sphere. Since a time for settlement was uniform for all spheres, larger spheres could take longer trajectories than small ones. The motion was interrupted or terminated if the sphere attained another sphere or the box floor. If the falling sphere hit a settled sphere, it rolled down in the steepest descent direction. The sphere rolling down could reach the same vertical position as that of its contact, or could encounter another settled sphere. In the former case the sphere was allowed to fall freely. In the later one, a path was determined by those two contact spheres. The displacement continued until the sphere was trapped in a stable position at a local minimum of potential energy. Since sedimentation was slow, no moving sphere could dislodge any settled one. However, the motion of a sphere was stopped in an unstable position if the vertical drop was greater than that determined from the force balance. An adjustable parameter representing the maximum reduction of the vertical coordinate controlled the entire process. Its value was set iteratively for the volume fraction of spheres to match the volume fraction of silicalite in the membrane. In order to reduce effects of box boundaries on the deposited layer, a bulk region of the entire box was only selected for the consecutive processing.

The next step of reconstruction was transformation of the off-lattice medium into a discrete (digitised) medium defined on a simple cubic lattice of size  $\hat{L}_x \hat{L}_y \hat{L}_z$  with spacing (lattice constant)  $a$ . Each small cube (voxel) was filled either with the silicalite phase or with the polyimide phase. Such two-phase digitised medium was further described in detail by the phase function,  $I(\mathbf{x})$ , for the polyimide phase

$$I(\mathbf{x}) = \begin{cases} 1, & \text{if } \mathbf{x} \text{ belongs to polyimide phase} \\ 0, & \text{otherwise} \end{cases}$$

Then the phase function was statistically characterised using microstructural descriptors, such as the volume fractions, the two-point probability function for the polyimide phase and the lineal-path functions for the polyimide and silicalite phases. These descriptors, being common to 2D and 3D space, were compared with those obtained directly from the images of 2D cuts through the membrane.

Finally, effective permeability of an arbitrary fluid in the digitised medium was estimated by exploiting the formal analogy between random walks and solutions of the Laplace equation. Permeability of the fluid in each phase was defined as the product of a diffusion coefficient and a solubility coefficient. A large number of random walkers taking discrete steps were considered and mean-square displacement versus time was calculated. Random steps were possible between neighbouring voxels of the opposite phases. For such steps, the probability associated with crossing the two-phase boundary had to equal a ratio of solubility coefficients given by Henry's law. Initial positions of the random walkers were chosen at random. But a relative number of initial positions were again defined as the solubility ratio. As input information, the simulation needed a ratio of diffusion coefficients and a ratio of solubility coefficients of the fluid in both phases. Experimental effective permeability was then compared with the theoretical prediction.