Computational Materials Science 89 (2014) 142–156

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Stochastic reconstruction of mixed-matrix membranes and evaluation of effective permeability

Pavel Čapek [a,*], Martin Veselý [a], Bohumil Bernauer [a], Petr Sysel [a], Vladimír Hejtmánek [b], Milan Kočiřík [c], Libor Brabec [c], Olga Prokopová [c]

[a] Institute of Chemical Technology, Prague, Faculty of Chemical Technology, Technická 5, 16628 Prague 6, Czech Republic
[b] Institute of Chemical Process Fundamentals of AS CR, Rozvojová 135, 16502 Prague 6, Czech Republic
[c] J. Heyrovský Institute of Physical Chemistry of AS CR, Dolejškova 3, 18223 Prague 8, Czech Republic

ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 21 February 2014
Accepted 1 March 2014

Keywords:
Microstructural descriptor
Simulated annealing
Sample-spanning cluster
Random walk simulation
Enhanced permeability

ABSTRACT

Microstructures of three mixed-matrix membrane samples made of polyimide and silicalite-1 particles were reconstructed using a stochastic reconstruction procedure. The samples differed in the volume fractions of silicalite-1 particles as follows: 0.166, 0.310 and 0.371. The reconstruction revealed the existence of percolation clusters of silicalite-1 particles in the two samples with the volume fraction of silicalite-1 greater than 0.3. In contrast, only the reconstructed microstructure of the first sample contained small clusters of silicalite-1 particles, which did not percolate along any direction. The results of this reconstruction were tested by simulating the random walk of CO_2 molecules in the reconstructed bodies and by predicting the effective permeability of CO_2. Both original and reconstructed membranes revealed a similar enhanced effective permeability, which exceeded predictions based on the effective medium approximations. Therefore, we suggest that clustering of the silicalite-1 particles was the primary cause of the permeability increase.

1. Introduction

In principle, the separation technology requires membranes with high permeability and selectivity. In this respect, pure dense polymeric membranes have reached their upper limits, represented by a line in the Robeson selectivity–permeability plot for any binary gas mixture [1,2]. For instance, dense membranes made of aromatic polyimides exhibit high separation efficiency for gaseous mixtures but low permeability for permanent gases and organic vapours [1]. The incorporation of solid fillers, such as microporous sorbents, into polymeric matrices seems to be a promising route towards composite membranes of improved overall separation efficiency, a concept proven in the mid-1980s [1–5]. Among microporous sorbents, zeolites are of particular interest.

Synthesis and application of composite membranes have been concerned with two issues: (i) poor adhesion between the phases associated with the formation of macroscopic voids at the phase interface (sieve-in-cage morphology) [1,2], and (ii) formation of rigidified polymer layers of reduced free volume at the phase interface deteriorating species exchange between the phases. An original way to improve the adhesion between the polyimide matrix and silicalite-1 crystals was introduced by Sysel et al. [6], who used (3-aminopropyl)triethoxysilane to modify the polyamic acid of a controlled mean molar mass. Another situation, possibly eliminating the desired effect of porous fillers, is the clogging of pores with strongly adsorbed species such as solvents. These observations suggest that membrane microphotographs and other types of microstructural information will contribute to the understanding of functional relationships between the membrane structure and membrane properties [7–13].

In general, a composite material consists of domains of different materials (phases) or of the same material in different states. Provided the properties of all phases are known, the issue is to determine the phase distribution within spatial domains that are much larger than molecules but much smaller than the characteristic length of a macroscopic sample, and the specific interactions on phase interfaces. In this sense, the ideal goal of microstructure analysis is to formulate mathematical models that will quantitatively account for all macroscopic (effective) properties, such as thermal and electrical conductivity, effective permeability and diffusivity, of real composites [14–18]. The great variety of composite materials, along with the spatial distribution and nature of the phases, make the comprehensive mathematical model a challenge. The recent progress of imaging and microscopy has led to the development of novel experimental methods that, with the aid of

---

* Corresponding author. Tel.: +420 220444407.
E-mail address: pavel.capek@vscht.cz (P. Čapek).

http://dx.doi.org/10.1016/j.commatsci.2014.03.003
0927-0256/© 2014 Elsevier B.V. All rights reserved.

more or less complex computer algorithms, are able to reconstruct the three-dimensional (3D) microstructure [14,15].

Serial tomography belongs to a group of invasive methods that take a set of images of two-dimensional (2D) cuts through a solid medium. Its thin parallel slices are sequentially removed by means of a microtome. Each emerging (polished) planar section is observed using a microscope that is capable of contrasting all material phases. Microscopic images are then stacked up so that the connectivity of objects belonging to the same phase can be established for each pair of successive sections. Since the 1990s, modern variants of serial tomography have evolved from its classical form [19], known to be laborious. For example, dual beam FIB-SEM instruments also enable serial sectioning and imaging and 3D reconstruction of microstructure. The ion beam is used to mill a duct in the bulk of a sample; subsequent automated milling and imaging occurs in situ of the bulk material, e.g. [9].

Adler et al. [20] and Adler [21] introduced a reconstruction method free of limitations on slice thickness. Unlike serial tomography, this method relies on images of planar sections whose distances and orientations are chosen completely at random, and on the statistical treatment of these images. A microstructural descriptor, a two-point probability function, is extracted from a set of images in order to be transformed into a 3D image (replica of real microstructure) by means of thresholding a Gaussian random field. Since only a statistical measure is used, properties of a replica do not often match those of real media [22]. Yeong and Torquato [23,24] proposed a stochastic reconstruction procedure based on principles of combinatorial minimisation and constrained by an arbitrary number of microstructural descriptors, specifically by the two-point probability function and by the lineal-path function for the void phase. Although this reconstruction procedure has been more successful, the resulting images do not always capture the long-range connectivity of pore space, namely for low porosity materials and particulate media. For example, Jiao et al. [25–27] compared the stochastic reconstruction methods based on simulated annealing (SA) and constrained by the two-point probability function, the lineal-path functions, the surface–surface correlation function, the surface–void correlation function, the pore-size functions, and the two-point cluster function. They found that the two-point cluster function was a superior microstructural descriptor, due to its sensitivity to long-range connectivity of pore space. Tahmasebi and Sahimi [28,29] proposed a new multi-point statistics algorithm for reconstruction of 3D porous media using a single thin section. Their method reproduces the long-range pore connectivity well and is very likely to overcome limitations of other multi-point statistics methods and stochastic reconstruction.

Čapek et al. [30] modified a method of stochastic reconstruction using SA constrained by the two-point probability function and the lineal-path function for both the void and solid phases. In addition, the two-point cluster function was indirectly used to adjust two parameters of the reconstruction procedure and to enhance pore space connectivity. The new method was capable of reproducing the void and solid phases as large clusters spanning the entire replicas (i.e. percolation clusters). Isolated clusters (non-percolating, not spanning a replica) formed minor volume fractions of both phases. Eight porous solids of different microstructures were selected to evaluate the performance of the new method [31]. For most of the solids, effective properties of the replicas obtained using the new method better matched their experimental counterparts than did the corresponding values derived from the microstructures reproduced using Yeong and Torquato's reconstruction method [23,24].

There are also non-invasive methods that visualise the 3D microstructure. X-ray computed tomography, particularly with a synchrotron X-ray source, is generally considered the most useful means of analysing the microstructure composite and porous media if objects of interest are approximately larger than 1 μm in diameter [32,33].

Determining the effective properties of two-phase and multiphase composites is a long-standing problem that has attracted the attention of famous scientists, including Maxwell, Rayleigh and Einstein. Since then, several analytical approaches to this problem have emerged, including popular effective-medium approximations. Unfortunately, these predictions of effective conductivity for dispersions in which the inclusions form large clusters are poor [15,34].

The increasing accessibility of microstructural analysis and high-performance computers makes numerical simulations that take the reconstructed medium as input information involving non-trivial microstructure features attractive. Such an approach, which is free of the limitations mentioned above, enables either the prediction of effective properties or the study of functional relationships between the microstructure and effective properties. Diffusion and heat conduction in the reconstructed medium can be simulated either by solving the differential equations for the concentration and temperature fields or by simulating Brownian motion [16–18]. The second approach takes advantage of more simple computer implementation, modest computer resources and sometimes better accuracy [16–18,35].

To our best knowledge, no comprehensive study that includes membrane preparation, reconstruction of its microstructure, measurement and prediction of effective permeability and comparison of both values has been reported to date. Therefore, it is worthwhile to carry out these steps and evaluate the performance of mathematical models of the microstructure and permeation.

The aim of this work is (I) to extend the reconstruction procedure recently developed for some disordered porous media [30,31] to two-phase composite materials, and (II) to exemplify this procedure on mixed-matrix membranes of the polyimide–silicalite type, prepared for this study. Specifically, the polymer phase is made of two monomers, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride and 4,4′-oxydianiline, and (3-aminopropyl)triethoxysilane as a terminating agent. Another aim is (III) to predict effective permeability of reconstructed bodies using random walk simulations and finally (IV) to compare experimental and predicted values of effective permeability of carbon dioxide with emphasis on the high concentrations of silicalite inclusions involving the percolating structures.

The paper is organised as follows. In Section 2, we give an overview of microstructural descriptors relevant to the paper and apply our recent stochastic reconstruction procedure [30,31] to composite materials. In Section 3, we outline our implementation of a random walk algorithm [18] and specify a theoretical framework for estimation of conductivity (permeability) of both membrane phases. Membrane preparation, imaging of polished sections of composites, image processing, calculation of microstructural descriptors, and measurement of effective permeability of mixed-matrix membranes are concentrated in Section 4. In Section 5, we show that reconstructed microstructures have the same selected statistical measures as the original 2D cuts through membrane samples. Furthermore, we characterise and analyse the microstructures to propose a hypothesis about the causes of elevated effective permeability. Finally, we compare effective permeability calculated using the random walk algorithm and its experimental counterpart.

2. Description of microstructure and its stochastic reconstruction

The structure of the digitised mixed-matrix membrane consisting of the two phases is completely defined in terms of the indicator function, $I^{(p)}(\boldsymbol{x})$, for the polyimide phase