Journal of Membrane Science 485 (2015) 42–47

Contents lists available at ScienceDirect

Journal of Membrane Science

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

On the threshold concentration of sticks providing formation of a percolating cluster in mixed matrix membranes

A.M. Grekhov *, Yu.S. Eremin

National Research Nuclear University MEPhI, Kashirskoe sh. 31, Moscow 115409, Russia

ARTICLE INFO

Article history:
Received 3 October 2014
Received in revised form
20 January 2015
Accepted 21 February 2015
Available online 20 March 2015

Keywords:
Mixed matrix membrane
Percolation threshold
Percolating cluster
Carbon nanotubes
CNT

ABSTRACT

At the present time, many publications on mixed matrix membranes (MMM) are concerned with the study of membranes containing nonspherical nanoparticles with high aspect ratios. Macroscopic characteristics of MMMs and their variations are known to be controlled by the parameters of a percolating cluster composed of incorporated particles in the host membrane. However, conditions providing the formation of percolating structures in films, the thickness of which is comparable to the dimensions of incorporated particles, can be appreciably different from the percolation scenario in isotropic infinite systems.

In this work, the Monte Carlo method is used to define the conditions providing the formation of a percolating cluster composed of sticks at varying concentrations of sticks in finite membrane and at different ratios between membrane thickness and dimensions of sticks. In the above systems, percolation-induced changes show a threshold character and take place in a narrow concentration interval. Parameters of the as-formed MMMs are found to be unstable and sensitive to both film thickness and aspect ratio of sticks.

1. Introduction

In recent years, many research works were devoted to mixed matrix membranes (MMMs) which are based on polymers containing incorporated nanoparticles, for example, TiO_2, ZnO, Al_2O_3, SiO_2, zeolites, nanofibers, and nanotubes [1]. Transport and selective characteristics of MMM are known to vary in a broad range depending on the type nature of a polymer and nanoparticles [2–6]. In these systems, working characteristics and performance of MMM change through different scenarios: for example, permeability increases with decreasing selectivity or, to the contrary, both permeability and selectivity tend to increase or gas permeability decreases but selectivity is preserved as in the classical filled polymers. This diversity in scenarios makes it possible to grasp why no universal approach to the description of transport mechanisms in MMM is available and why all existing models for the calculation of the working parameters of MMM are being continuously revised and refined. Characteristics of MMM are known to be controlled not only by the type and content of incorporated nanoparticles but also by the parameters of diverse structures produced by particles in host membranes [7–11]. Both transport and selective characteristics of membranes are dramatically changed when concentration of the incorporated nanoparticles exceeds a certain critical threshold and a percolating cluster is formed whose dimensions are bigger as compared with the membrane thickness. Therefore, experimental studies and numerical simulation of the conditions providing the formation of a percolating cluster and characterization of its properties present a challenging task for further development of the MMM production technology.

At the present time, the conditions providing the formation of a percolating cluster were studied by the computer simulation experiments for continuum 2D and 3D systems, and these studies showed that the threshold concentration markedly depends on the geometrical characteristics of the particles, and this parameter nonlinearly decreases with increasing their aspect ratio [12–15]. This decrease in the percolation concentration of particles was experimentally proved for MMMs containing carbon nanotubes with different aspect ratios [1,7–9,16,17]. This observation has its evident practical value because, with decreasing content of incorporated particles, their distribution in MMM becomes more uniform and the technology of MMM production is simplified. However, for the particles with higher aspect ratios, variations in the characteristics of the corresponding MMM at the percolation threshold are far from being stable [18–25]. This behavior can be explained by the interaction of the particles in the host matrix and by their agglomeration which entails the breakdown of the percolation structure in the membrane. We expect that, in

* Corresponding author. Tel.: +7 916 507 48 91.
E-mail address: amgrekhov@mephi.ru (A.M. Grekhov).

http://dx.doi.org/10.1016/j.memsci.2015.02.046
0376-7388/

addition to the properties of the particles, percolation parameters are controlled by the geometry of the membranes.

Parameters of percolation structures composed of particles are usually analyzed for anisotropic infinite systems but membranes are the films whose thickness is appreciably lower as compared with their linear dimensions, and the size of incorporated particles can be comparable to the film thickness. Changes in transport characteristics are known to be provided by the formation of a percolating cluster in the direction normal to the membrane surface. Then, the parameters of the as-formed percolating cluster should be different from the anisotropic case in quadratic matrices. In this work, we studied the probability of the formation of a percolating cluster composed of sticks in *rectangular matrices* with a length of a shorter side of 30 relative units and with a length of a longer side varying from 30 to 1000 relative units. The specific features of the formed percolating cluster can be invoked to explain the observed instability of transport characteristics of MMM which is observed at the percolation concentration of the particles in the host membrane. First, the percolation threshold concentration and the dimensions of the percolating cluster nonlinearly decrease with increasing width of the host matrix or with increasing length of sticks. Second, at the percolation transition, the dimensions of the percolating cluster are nearly zero but markedly increase only when the concentration of sticks exceeds a certain percolation threshold. Therefore, even minor changes in the concentration of sticks or in the dimensions of the host matrix can exert a marked effect on the parameters of the percolation structure which controls the bulk characteristics of the corresponding MMM.

2. Numerical simulation

For the Monte Carlo simulation of the percolating cluster, the following standard algorithms were applied: the Mersenne twister algorithm for the definition of coordinates of the center of sticks and their orientation in the host matrix [26], the Hoshen–Kopelman algorithm for the identification whether individual sticks belong to the finite clusters [27] or to the percolating cluster [28,29]. Numerical simulation is performed for a rectangular matrix with $W \times H$ dimensions where a given number of sticks with length L and width d are distributed at random, and their connectivity provides the formation of clusters. When the matrix is occupied by N sticks, all sticks are assigned to certain clusters, and the percolation condition is defined or, in other words, the condition for the formation of a cluster which contains the sticks crossing both longer sides of the matrix. For each concentration of sticks, one thousand generations of the matrix occupation is performed, and the probability of percolation reads as $p = m/1000$, where m is the number of generations in which a percolating cluster is formed. For percolation cases, the strength of the percolating cluster is calculated as $P_\infty = N_\infty/N$, where N_∞ is the number of sticks in the percolating cluster, and N is the overall number of sticks. We also calculated the concentrations: the area of the host matrix occupied by sticks is $x = N \cdot L \cdot d/W \cdot H$ and the area occupied by the sticks involved in the percolating cluster is $x_\infty = N_\infty \cdot L \cdot d/W \cdot H$.

To verify the calculation procedure, the percolation parameters for a finite matrix occupied by randomly oriented squares and circles are estimated. In the calculations, the percolation threshold is defined as the ratio of the overall area of all particles to the matrix area upon the formation of the percolating cluster. As overlapping of particles is ignored, the percolation threshold can exceed unity. Table 1 lists the calculated values of the percolation threshold and these values are seen to differ from the accurate published data [30] by not more than 0.001 units, and this difference implies that deviation of our estimates is below $\delta \sim 0.1\%$. This discrepancy can be diminished with increasing number of matrix occupation generations m ($\delta \sim M^{-0.5}$ [30]) or with increasing matrix dimensions L ($\delta \sim L^{-\nu}$, where ν is the index defined by the system parameters [31]). For example, for the simulation of percolation parameters for sticks in a bigger matrix, the deviation of the calculated values of percolation threshold from the literature data is below 0.02%. However, from the applied viewpoint, estimation of the percolation structure characteristics with an accuracy of 0.1% is sufficient for most experimental works on the MMMs where the volume concentration of the particles in membranes is accurately controlled.

Table 1
Percolation threshold and estimation (calculation) accuracy.

Sources and deviation	Circles	Squares	Sticks
Literature data [30]	1.12808737 (6)	0.9822723 (1)	5.6372858 (6)
Our calculations	1.127 ± 0.001	0.981 ± 0.001	5.636 ± 0.001
Relative deviation, δ	8.8×10^{-4}	1×10^{-3}	1.8×10^{-4}

3. Results and discussion

Simulation experiments are performed as follows: rectangular matrices with height $H=30$ and width $W=30$, 60, 90, 150, 300, 600, and 1000 are occupied with sticks with length $L=2$, 3, and 4 (in dimensionless units) and with thickness $d=0.001$. Fig. 1a shows the probability of the formation of a percolating cluster at different concentrations of sticks. With increasing width of the host matrix, the probability of the formation of the percolating cluster becomes non-zero at lower concentrations, and the concentration interval, where the percolation probability changes from 0 to 1, decreases. In other words, as the matrix width increases, the percolation threshold becomes more pronounced, and the whole system becomes more susceptible to changes in the concentration of sticks. For example, for sticks with a length of 2, as the matrix width increases from 30 to 1000, the width of the percolation transition decreases nearly by a factor of two. With increasing length of sticks, the percolation threshold is also seen to be markedly decreased. For sticks with a length of 4 at the concentration $x \sim 0.002$, the percolating cluster is assuredly formed in a 30×30 square matrix whereas, for sticks with a length of 2, the percolation probability approaches zero even for the matrix with a width of 1000.

Fig. 1b shows the strength P_∞, which characterizes the maturity of the percolating cluster. When P_∞ is low (even when the percolating cluster is formed), most fraction of the matrix contains only finite clusters and exists in the pre-percolation state. Similar to the probability of percolation, as the matrix width increases, changes in strength become more pronounced. The percolating cluster in the 30×30 matrix contains less than 35% of the overall amount of sticks. When the matrix width is 1000, this strength is achieved at the concentrations when the probability of percolation is $p > 0.3$. However, when the probability is $p > 0.6$, the effect of the matrix width on the strength of the percolating cluster becomes less pronounced. As the length of sticks increases from 2 to 4, the strength of the percolating cluster at fixed concentrations decreases. For example, when the concentration of sticks is ~ 0.0025, nearly all sticks with a length of 4 are organized into a percolating cluster. However, at the same concentration of sticks with a length of 2 in the matrix with a width of 30, the strength is $P_\infty < 0.5$. For the matrix with a width of 1000, less than 0.1% of all sticks are involved in the percolating cluster. This susceptibility of the percolating cluster critically controls the macroscopic