Journal of Membrane Science 543 (2017) 328–334

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Exploration of the nanostructures and separation properties of cross-linked mixed matrix membranes using multiscale modeling

Tzu-Hao Chen[a], Yi-Rui Chen[a], Liang-Hsun Chen[a], Kai-Shiun Chang[a], Yi-Feng Lin[b], Kuo-Lun Tung[a,*]

[a] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan
[b] R & D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chungli 320, Taiwan

ARTICLE INFO

Keywords:
Molecular dynamics
Organic-inorganic mixed matrix membranes (MMMs)
Pervaporation
Crosslinking
Multiscale modeling

ABSTRACT

A new simulation scheme was established for strategically constructing cross-linked organic-inorganic mixed matrix membrane materials. This is a multiscale method using customized programming to effectively model complicated nanostructures. The effects of hybrid fillers in the chitosan/graphene oxide composite membranes are systematically elucidated at the molecular scale. Observed from the radial distribution function analysis, the significant enhancement of the separation performance in the dehydration of alcohols can be attributed to the stabilized polymer chains and the conspicuous increase in the water adsorption from mixing with graphene oxide sheets. Results show that the simulated models agree well with the experimental works in membrane density and transfer behavior of vapor molecules, which demonstrate that the modeling tools can be applied to evaluate the performance of cross-linked mixed matrix membranes, and to design various combination of hybrid membranes.

1. Introduction

Pervaporation is an effective membrane separation process for the dehydration of alcohols that has attracted wide attention in the development of high-performance selective membranes [1]. Mixed matrix membranes (MMMs) with organic polymeric matrices and inorganic fillers are regarded as next-generation membrane materials to overcome the inevitable trade-off between permeability and selectivity [2]. To prepare state-of-the-art MMMs for water/ethanol separation, polymer matrices with high water affinity [3,4] (e.g., polyvinyl alcohol, polyelectrolytes, etc.) are employed, and strong molecular sieving nanofillers [5,6] (e.g., ZIFs, carbon molecular sieves, etc.) are chosen as synergistic additives. In particular, chitosan (CS) and sodium alginate have commonly been adopted as the polymer matrices due to their superior selective performances [7–9] after cross-linking, because the cross-linkers can maintain their selectivity by lowering the swelling of the hydrophilic polymer chains [10]. Graphene oxide (GO) laminated sheets were found to have unique water transport channels [11,12] and thus are taken as the best 2D fillers for pervaporation [13]. These composites were successfully fabricated as flat sheet [14] and hollow fiber membranes, which have taken the leading positions in pervaporation processes [15–17].

Many theoretical models have been developed in recent years to predict the performances of various hybrid membranes [18]. Maxwell model is a classical expression for describing ideal MMMs with simple equations [19], but it was demonstrated to have accuracy only by low volume fraction of fillers [20,21]. Therefore, diverse modified models are developed in succession to predict the permeation properties of MMMs consisting of more complicated morphologies [22–25]. Molecular simulation techniques help us specifically study the various interaction among different materials. As well as the powerful tool to test the performance of new products, discover potential problems, or make prediction of different applications. As the computational science make steady progress with concomitant drop in price, modeling methods are studied to be applied on high-performance composite materials [26–29]. Cross-linked nanostructures in modeling work have been developed for several years, polymeric framework in certain degree of cross-linking can be cleverly achieved through a stepwise procedure [30]. By characterizing physical properties afterward, the corresponding cross-linking structure will be sieved out.

However, few simulations have been performed to explore the combination of materials with intricate nanostructures. It is under development to evaluate a fresh combination of hybrid material, and the effects of hybrid frameworks still remained unclear. In order to develop more promising combinations of different materials, a new simulation plan was proposed to study the structural arrangements, and discern the

* Corresponding author.
E-mail address: kuolun@ntu.edu.tw (K.-L. Tung).

http://dx.doi.org/10.1016/j.memsci.2017.08.061
Received 30 April 2017; Received in revised form 24 August 2017; Accepted 26 August 2017
Available online 30 August 2017
0376-7388/

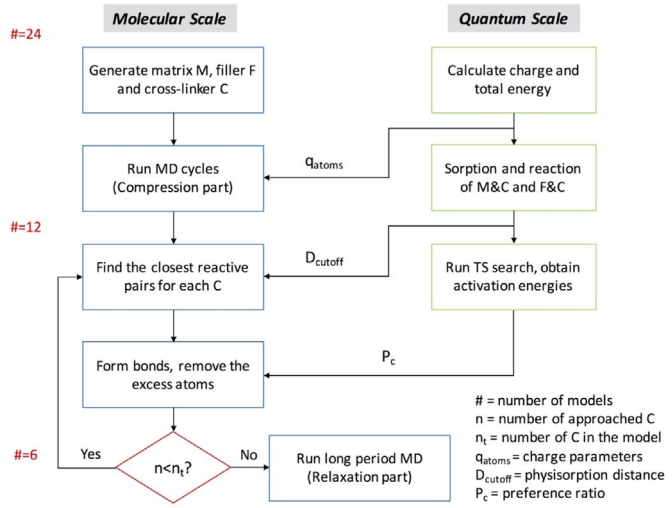

Fig. 1. Modeling scheme used in this study combined with molecular and quantum scale.

effects of fillers in fabricating MMMs. Besides, a simulation procedure is developed by computational programming to effectively build the cross-linked structures of MMMs at molecular scale. Which can implement the cross-linking process automatically and combine the 2D inorganic fillers with the polymeric matrix, fabricating the MMM frameworks reasonably.

2. Theoretical method

A scale-combined modeling scheme was established in Fig. 1, which took molecular dynamics (MD) with three pivotal parameters obtained from quantum mechanical calculations: (1) the charge parameters, (2) the reactive physisorption distance, and (3) the preference ratio for the cross-linking reactions. The modeled CS/GO MMM was compared with a pure CS polymeric membrane and a cross-linked CS polymeric membrane. A customized constructing method with cross-linking processes was designed by Perl computational programming, where glutaraldehyde (GA) is chosen as the cross-linker. All of the calculations were performed using Materials Studio 6.0 (Accelrys Inc., San Diego).

2.1. Model construction

First, the activation energies of the two cross-linking reactions were calculated from transition state search [31] to decide a preference ratio of the GA-CS reaction to the GA-GO reaction, and the physisorption distances were set as their respective reactive radii. The transition state searching paths found by the CASTEP module are shown in Fig. 2, the two cross-linking structures can be found in Fig. S2. After the optimized MD processes, each of the three membrane materials was completed under the condition of 1 bar and 298 K in six independent models. Fig. S3 shows the time courses of the constructing densities during the MD simulation scheme. This modeling method can be adjusted easily according to the different cross-linking reactions. In this study, 7 × 7 graphene sheets are adopted as the filler, of which each side includes 7 benzenes. The side length of the graphene sheet is around 21 Å, overpassing the maximum electrostatic cutoff distance (18.5 Å) in the simulation algorithms. That is, as experimental situation, the carbon atoms on opposite margin will not have interaction with each other. Under the limitation of molecular simulation, it is a cost-effective way to approximately realize the properties of larger size GO in common. The oxide groups were randomly added on according to the actual C/O ratio from experiments [32]. For polymeric phase, three polymer chains were adopted in the membrane models, and each chain comprises 100

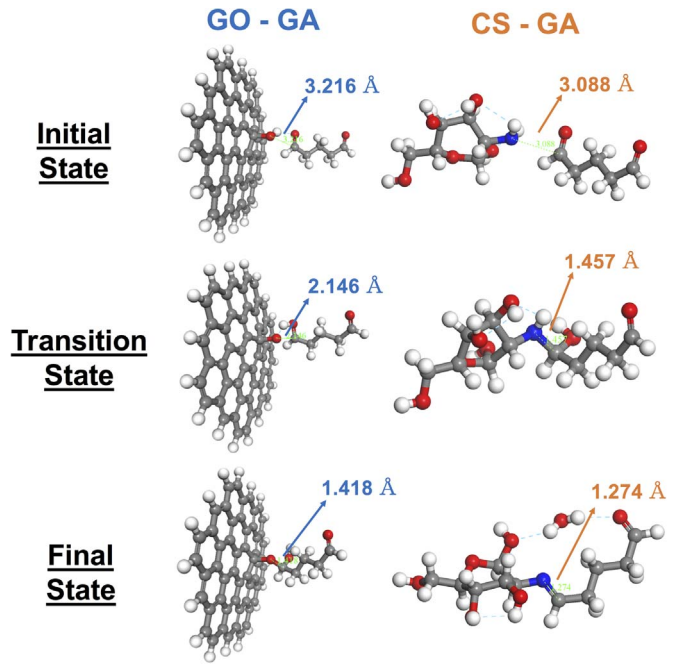

Fig. 2. The mechanisms of the two cross-linking processes. (gray atom: carbon, white atom: hydrogen, red atom: oxygen, blue atom: nitrogen). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

repeat units of the CS monomer (molecular weight = 16,118 g/cm^3). To avoid the catenation of polymer chains, 5 wt% of methane molecule was added in as inert gas in the beginning of the MD simulation processes. More details of the model construction are included in the Supporting information.

2.2. Physical property analyses

The end-to-end distance of polymeric chains can be regard as a reliable parameter to evaluate the rigidity and the oscillation of the membrane structures [33]. Which is a really simple way to quickly compare the structural stability of different membranes. With the atomic coordinates recorded in each simulation time step, the end-to-end distance of CS chains in both cross-linked membrane models were measured during a long period MD process to quantize their packing fixity.

The dihedral angle distribution, and the pore size distribution are conducted to further explore the hybrid membranes. To deeply investigate the material structures, the pore size distribution (PSD) was obtained using a statistical image analysis algorithm, which is based on the Euclidean distance transform [34], in MATLAB programming as shown in Fig. 3. The molecular models were divided into ten slices in each axis, and the R_max approach [35] was adopted to calculate the amounts and sizes of cavities in each cross-sectional image. For each cross-sectional image, the area occupied by cavity size elements was converted into the equivalent circle, so the effective pore diameters and the pore size distribution of different membrane models can be obtained from the average result of the six independent models.

Besides, the transport behavior of vapor molecules across a membrane can be influenced by their diffusivity and solubility on the membrane. In this study, all the analyzed properties were averaged from the constructed six independent models of each membrane. Other details of the theoretical calculations and the analyses are included in the Supporting information.