01 Sep 2012

Design and Characterization of Asymmetric Cross-Linked Polymer Membranes by Molecular Dynamics Modeling and Simulations

Jee-Ching Wang
Missouri University of Science and Technology, jcwang@mst.edu

Athanasios I. Liapis
Missouri University of Science and Technology, ail@mst.edu

Recommended Citation

J. Wang and A. I. Liapis, "Design and Characterization of Asymmetric Cross-Linked Polymer Membranes by Molecular Dynamics Modeling and Simulations," *Procedia Engineering*, vol. 44, pp. 173-174, Elsevier, Sep 2012.
The definitive version is available at https://doi.org/10.1016/j.proeng.2012.08.348

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 173 – 174

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OA55]

DESIGN AND CHARACTERIZATION OF ASYMMETRIC CROSS-LINKED POLYMER MEMBRANES BY MOLECULAR DYNAMICS MODELING AND SIMULATIONS

J.C. WANG*, A.I. LIAPIS

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY, USA

Membranes are widely used in separation processes and are often categorized by different factors such as the materials from which are made of, their shape and structure, as well as by the physicochemical properties they possess and which enable them to have appropriately desired interactions with the targeted molecules of the solutes and of the solvent. A great deal of effort has been devoted to modifying these properties in order to improve the membrane performance or make them to become functional in specialized applications. One of the most important properties in determining the performance and application of a membrane is the porous structure and more specifically the distributions in the membrane of the pore sizes and of the pore connectivity. In polymer membranes, the porous structure is determined mainly by the mutual interactions between the conformationally and configurationally flexible polymer chains, and the membrane structural and dynamic properties can be further modified by physical and/or chemical means such as cross-linking which covalently connects the polymer chains together. When the pore sizes are made to be characteristically dissimilar in different parts of a membrane, the result is an asymmetric membrane that, in contrast to conventional membranes with comparable pore sizes throughout, can provide additional advantages including fast and consistent molecular transport while requiring lower in magnitude gradients of externally applied forces. From both fundamental and practical points of view, asymmetric polymer membranes can be prepared by systematically utilizing cross-linkers differing in sizes and/or different extents of cross-linking in different parts of the membrane. While this appears to provide a plausible strategy for the molecular design of membranes, its practical feasibility still remains to be realized and requires detailed characterization. We present in this work a proof-of-concept study that employs the molecular dynamics (MD) modeling and simulation methodology to construct and characterize composite asymmetric polymer membranes formed by dextran chains and cross-linked by polyols. This selection of model membrane systems is based on the rationale that dextran and polyols provide desirable biocompatibility and good solubility in water, which have led to many bio-related applications.

The model asymmetric membranes are consisted of two polymer thin films separated from each other but fastened together by a porous skin layer represented by a curved interface with sinusoidal features and periodic pores. During the construction of the model membrane systems, the dextran chains are grafted with different surface densities onto the two different sides of the skin layer in the proximity of the sinusoidal peaks, while the valley regions are left with open holes to permit the transport of solvent and solutes between the two sides. Selected numbers of cross-linking polyols with appropriate lengths determined by the dextran densities have one end of the polyols bonded to the grafted dextran chain and the other end free and given specific interactions with other free ends. When two free polyol ends come within a short distance from each other, a bond is formed between them and a cross-linking interaction is completed. After the extent of cross-linking reaches a pre-specified level, the cross-linking interactions are stopped and the noncross-linked polyols are eliminated from the simulation system before it enters the phase of equilibration. This unique procedure for constructing cross-linked polymer systems yields realistic structures with low internal stresses and good computational efficiency. In addition, particular distributions of the cross-linkers may provide additional advantages to the membrane, which can be readily studied by this cross-linking strategy. After equilibration, the pore structures are characterized directly in terms of the distributions of the number of pore openings, pore radii, and pore volumes by dividing each of the polymer thin films into two levels of cubic lattices at the angstrom level and utilizing thin

doi:10.1016/j.proeng.2012.08.348

disks of varying sizes at each lattice point. The degree of pore connectivity is then ascertained by the intersection between distribution curves that represent pores of different size ranges.

The interaction energetics and effective mass transfer coefficients of water molecules and their distributions on the two different sides of the asymmetric membranes are evaluated and are used as an indication of the relative difficulty or ease associated with water sorption and desorption, which represent parts of the mechanisms underlying the functioning of polymer membranes. In general, the pores are larger in diameter and the polymer film is more flexible on the side of the asymmetric membrane having a lower dextran density. Within a distance corresponding to approximately three water molecular diameters from the dextran chains and the polyol cross-linkers, water molecules, in particular those adjacent to the dextran chains and cross-linkers, are found to have greater interaction energetics and, thus, are more strongly bound, and their mass transfer coefficients are significantly reduced in magnitude. With larger in diameter pores and more weakly bound water molecules, faster transport, sorption, and desorption rates of water and potential solutes of interest can be obtained on the side of asymmetric membranes having lower densities of dextran polymer chains. Furthermore, to investigate the mechanical property of the polymer thin films, selected forces/stresses are applied to the water molecules in the regions immediately above the dextran chains, and the polymer films having high densities and/or higher levels of cross-linking are found to be more resilient and exhibit smaller strains in response to the mechanical stresses.

By further changing the length of the cross-linking polyols and the number of cross-linkers per dextran chain on both sides of the asymmetric membranes, systematic changes in the resulting porous structures are realized and are summarized in a form which can provide a useful guidance for practitioners. Compared to most of the relevant modeling and simulation studies, our model systems are completely off-lattice and consisted of genuine thin polymer films and an explicit porous support, and, thus, more realistic and more advantageous. The MD modeling and simulation studies presented in this work can also be extended to explore in the future additional aspects and new applications of asymmetric polymer membranes, including further modification and specialization of the porous structures by conferring adsorption capabilities through the immobilization of ligands and by studying the mass transfer mechanisms and determining the values of the mass transfer coefficients of different solutes for bioseparation (i.e., membrane chromatography) purposes.

Keywords: Asymmetric membrane, Cross-linked polymer films, Molecular dynamics modeling and simulations, Molecular design and characterization