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The effect of bioadhesive on the interfacial compatibility and pervaporation performance of composite membranes by MD and GCMC simulation

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ABSTRACT

Combing molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulation, the effect of bioadhesive transition layer on the interfacial compatibility of the pervaporation composite membranes, and the pervaporation performance toward penetrant molecules were investigated. In our previous experimental study, the structural stability and permeability selectivity of the composite membranes were considerably enhanced by the introduction of bioadhesive carbopol (CP). In the present study, the interfacial compatibility and the interfacial energies between the chitosan (CS) separation layer, CP transition layer and the support layer were investigated, respectively. The mobility of polymer chains, free volume in bulk and interface regions were evaluated by the mean-square displacement (MSD) and free volume voids (FFV) analysis. The diffusion and sorption behavior of water/ethanol molecules in bulk and interface regions were characterized. The simulation results of membrane structure have good consistency, indicating that the introduction of CP transition layer improved the interfacial compatibility and interaction between the separation layer and the support layer. Comparing the bulk region of the separation layer, the mobility and free volume of the polymer chain in the interface region decreased and thus reduced the swelling of CS active layer, revealing the increased diffusion selectivity toward the permeated water and ethanol molecules. The strong hydrogen bonds interaction between the —COOH of the CP transition layer and water molecules increased the adsorption of water molecules in the interface region. The simulation results were quite consistent with the experimental results.

1. Introduction

Pervaporation membrane as a polar membrane can be divided into homogeneous membrane and composite membrane according to its structure. The homogeneous membrane is generally dense, which results in the resistance of the components through it is large and the permeation flux is usually small. This kind of membrane is chiefly used in the laboratory, but not suitable for the practical production. The composite membranes were composed of a thin active layer and a porous support layer with different materials, respectively. Such combination of two independent layers would aims to obtain high permeation flux, high separation selectivity and structural stability. So that it would be more suitable for large-scale industrial application. The first GFT membrane used in industrialization process was a composite membrane consisting of maleic acid crosslinked polyvinyl alcohol as the separation layer while polyacrylonitrile as the support layer. The existing commercial membranes such as VP-31, VP-43, CF-23, PERVAP2510 [1], PERVAP2201, CMC-CA-01, CMC-CE-01 [2], PTFE [3], PolyAn and Sulzer Pervap membranes [4] and other series were all composite membranes.

Besides the permeation flux and separation factor, the structural stability of composite membrane is also an important index for evaluating membrane performance. Materials usually used as the separation layers of composite membrane, such as chitosan (CS), polyvinyl alcohol (PVA) and sodium alginate (SA) etc., are relatively hydrophilic. That used as ultrafiltration membranes for the support layers of composite membrane, such as polyacrylonitrile (PAN), polysulfone (PS) and cellulose acetate (CA) etc., are relatively hydrophobic. The surface tension of the two kinds of materials

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Nomenclature

Symbol	*description*
δ	Solubility parameter
E	Cohesive energy
E_{int}	Interfacial interaction
$E_{int,H\text{-}bind}$	H-bind interfacial interaction hydrogen bonding components
$E_{int,vdW}$	Interfacial interaction van der waals force component
$E_{int,electrostatic}$	Interfacial interaction in the electrostatic force component
MSD	Mean square displacement
D	Diffusion coefficient
FFV	Fractional free volume
R_{H2O}	The kinetic radius of the water molecules
R_{EtOH}	The kinetic radius of the ethanol molecules
$r_i(t)$	Positions of atom i at time t
$r_i(0)$	Positions of atom i at time 0

used as the separation layer and the support layer is usually different, for example, the critical surface tension of PVA and PAN is 37×10^{-3} N m^{-1} and 50×10^{-3} N m^{-1}, respectively [5]. It will lead to a high interfacial tension and a low interfacial interaction, consequently, results in a poor compatibility of the two layers. In addition, the swelling behavior is a common problem in the pervaporation process. If the swelling ratio of separation layer and support layer is inconsistent, a greater stress will be generated on the interface of the two layers, and if the stress exceeds a "critical point" (which is determined by the interaction between two adjacent materials) will lead to membrane disintegrated. Therefore, the interfacial compatibility between the separation layer and the support layer is critical to the structural stability and separation performance of the composite membrane.

At present, there are three main ways to improve the structural stability of the composite membrane: multilayer structure [6,7], separation layer crosslinking modification [8–10] and integrated structure strategy [11,12]. In which, multilayer structure strategy refers to coating one or a plurality of middle layers on the support layer, which possesses good compatibility with the separation layer and the support layer. Huang et al. [6] inserted an intermediate layer of mildly crosslinked hydroxyethyl cellulose between the CS separation layer and PS support layer. Zhao et al. [7] inserted a transition layer of polycarbophil calcium between the CS separation layer and the PAN support layer, and investigated the effect on the structure stability of the composite membrane. It was found that the inserted middle layer played a buffer between the separation layer and the support layer, which reduced the difference in the surface tension of the adjacent layer and enhanced the interfacial interaction, thus the structural stability of the composite membrane was improved.

Interfacial compatibility and interaction play an important role in determining the structural stability of the pervaporation membrane. It is the simplest and most direct way to enhance interfacial interaction by using adhesive. Which, the bio-adhesive outperform the traditional adhesive in many areas, such as they do not require high temperature and pressure to achieve rapid bond, and they are non-poisonous. Inspired by bioadhesion, many researchers use mussel-adhesive-mimetic materials to fabricate structurally stable composite membrane, such as the introduction of bioadhesive polydopamine into the composite membranes for improving interfacial stability [13–15]. In our previous study [16], the bioadhesive carbopol (CP) was introduced into the composite membrane and achieved good separation properties of ethanol and water molecules. However, the interfacial adhesion mechanism of the bioadhesive, and the reason for the improvement of the structural stability as well as the separation performance have not been well obtained by experimental means.

Molecular simulation as an effective tool has been widely used in the organic membrane research. It could not only simulate the experimental process in reality, but also be applied to study the molecular structure of macromolecules, the interaction between macromolecules and the diffusion behavior of penetrant molecules in the separation membrane [17,18]. Sandoval et al. [19] studied the interfacial interactions of CS with the blends of PVA and polyhydroxyethyl methacrylic acid (PMA), respectively. The results revealed that the interaction between PVA and CS is predominantly with the hydroxymethyl, while for the PMA its predominantly interaction is an amino group. Aminabhavi et al. [20] investigated the interaction between polymethyl methacrylate and polyacrylonitrile, polyvinylidene fluoride, polyethersulfone, polycarbonate as well as other polymers, calculated the solubility parameters of its oligomers, and the simulation results agreed well with the experimental data. Zhang et al. [21] investigated the swelling properties of PVA in aqueous solutions with different water contents, the intrinsic relationship between the microstructure of swollen PVA and water or ethanol in the membrane was analyzed. It was found that the free volume reduced as the degree of crystallinity of the PVA decreased. Water molecules adsorbed around the hydrophilic hydroxyl chain in PVA, forming hydrogen bonds, and the diffusion coefficient of water and ethanol increased as the increase of swelling degree. Jiang et al. [22] studied the interfacial interaction between the gelatin active layer and the support layer by molecular dynamics (MD) simulation.

The objective of this study is to investigate the effect of introducing bioadhesive CP (the molecular structure is shown in Fig. 1) on the interfacial compatibility and pervaporation performance of composite membranes by MD and Grand Canonical Monte Carlo (GCMC) simulation. The most common CS was used as the separation layer of composite membrane, bioadhesive CP was introduced as the transition layer, and the cellulose acetate (CA) as well as hydrolysis modified polyacrylonitrile (HM-PAN) served as its support layer, respectively. Different models including the bulk region of the separation layer, the interfacial region and the support layer region were constructed. The interfacial compatibility was characterized by the quantitative calculation of solubility parameter and interfacial energies. The membrane structures characteristics in the region of bulk and interface were respectively evaluated, the diffusion and adsorption behavior of the penetrant water and ethanol molecules in the bulk phase of separation layer and the interface phase were also investigated. The simulation results were compared with the experimental results to verify the validity of the simulation methods, and in turn, the simulation results also provide explanations and supplements for some phenomena in the experiment process.

2. Simulation details

2.1. Model building

The model construction and MD simulation were conducted in Materials Studio soft (Accelrys Inc., San Diego, CA, U.S.A.). In this study, the main homogeneous membrane model of CS, CP, CA and HM-PAN membranes were constructed, respectively. The polymer chains were all consisted of 200 repeating units, and a structural model of 1 polymer chains with periodic boundary conditions was constructed, respectively. Hydrolysis modified polyacrylonitrile membrane has been investigated by many researches using experiment and simulation methods. When PAN supports undergo hydrolysis in a NaOH solution, their —CN groups can be converted