The Lifshitz-van der Waals acid-base theory assisted fabrication of MFI-containing mixed matrix membranes for gas separations

Sunghwan Park[a,1], Eunhee Jang[b,1], Heseong An[a], Wansuk Choi[b], Jeong-Hoon Kim[c], Jung-Hyun Lee[b,*], Jungkyu Choi[b,**], Jong Suk Lee[a,***]

[a] Department of Chemical and Biomolecular Engineering, Sogang University, 35, Baekbeom-ro, Mapo-gu, Seoul 04107, Republic of Korea
[b] Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea
[c] Greenhouse Gas Separation and Recovery Research Group, Carbon Resources Institute, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea

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ABSTRACT

A zeolite-containing mixed matrix membrane (MMM) is an attractive option to overcome the performance limits of polymeric membranes for large-scale gas separations. The poor interfacial adhesion between zeolites and polymers, however, should be addressed to realize the excellent separation performance of zeolites on large industrial scale. Herein, the interfacial void-free MMMs with incorporation of intact MFI type zeolite particles were successfully prepared by applying the Lifshitz-van der Waals acid-base theory for the selection of the appropriate polymer matrix. Our simple, but systematic approach was based on the adhesion force between MFI particles and a surrounding polymer matrix. The relatively high Lewis basicity of cellulose acetate (CA) leads to highest adhesion force with MFI particles among the tested polymer matrices, suppressing interfacial void formation. In addition, a careful analysis revealed that any residual surfactants on the surface of MFI particles are detrimental to fabricate interfacial void-free MMMs. Single gas (i.e. N_2 and NF_3) transport in the CA/MFI MMMs were characterized by changing the concentration of MFI particles up to 30 wt%. N_2 permeability of CA/MFI MMMs was improved by as much as 304% compared to that of bare CA membranes with maintaining N_2/NF_3 permselectivity. Furthermore, gas transports in CA/MFI MMMs by varying the size of MFI particles from 0.2 through 0.6 up to 1.5 μm were analyzed by using the Lewis-Nielsen model. Our systematic theory-based guidance can be utilized to offer the appropriate polymer candidates for the zeolite-containing MMMs for high performance gas separations.

1. Introduction

Membrane-based gas separation technology is promising as alternative to conventional gas separation methods such as adsorption and distillation because membranes require less space as well as less energy [1]. Especially, polymeric membranes have been most widely used due to their cost competitiveness and high processability [2]. However, the inherent trade-off between permeability and selectivity with an upper bound limit deters their consideration for use in many applications [3]. On the other hand, inorganic membranes show technically superior separation performances via the molecular sieving of highly selective molecular-sized pores [4], but the large-scale membrane fabrication of such materials has yet to be addressed for industrial application. With

those in mind, embedding and dispersing molecular sieves including zeolite [5], silica [6], and metal-organic framework (MOF) [7] in a polymer matrix, known as mixed matrix membranes (MMMs), are attractive to overcome the upper bound limit, while maintaining the high processability suitable for scale-up at larger dimensions.

Conventionally, zeolites received considerable attention as molecular sieves due to their accurate pore shape and size-based discrimination of gas molecules with good thermal and mechanical stabilities [8]. It is, however, still challenging to realize their molecular sieving function in the associated MMMs especially due to the interfacial voids between the polymer matrix and zeolite particles [9,10]. Substantial efforts have been made to resolve the interfacial adhesion issue of zeolite-containing MMMs by either modifying the surface of
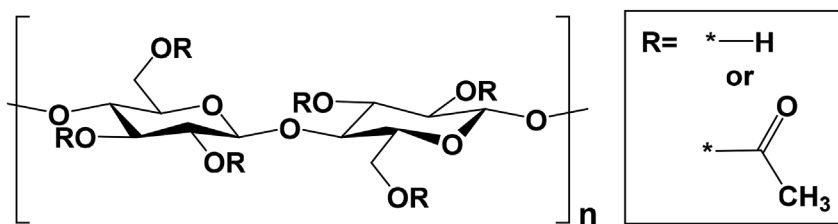

(a) Cellulose acetate (CA)

$R= *—H$ or
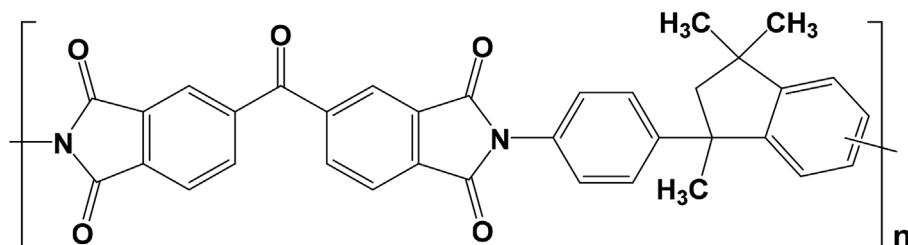
(b) Polyimide (PI)
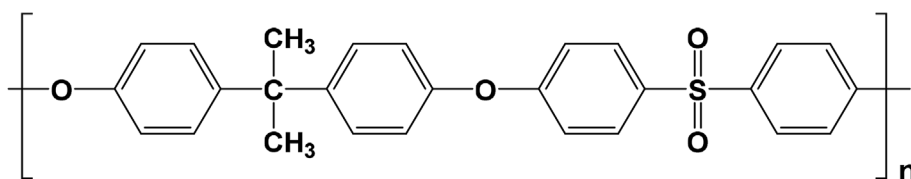
(c) Polysulfone (PSf)

zeolites or promoting thermal relaxation-induced wettability of polymeric chains [11,12]. For instance, silane coupling agents with functional end groups were attached to the surface of zeolites via hydrolysis and the functional groups were utilized to enhance the interaction between the external surface of zeolites and polymeric chains. Specifically, amino silanes such as (3-aminopropyl)diethoxymethylsilane (APDEMS) [9] and (3-aminopropyl)triethoxysilane (APTES) [13] are commonly adopted as a coupling agent since they are bulky enough not to penetrate into the pore of zeolites while promoting interactions between polymeric chains and zeolites. Also, Shu et al. [14] suggested the formation of whisker-like nanostructures of $Mg(OH)_2$ on the surface of zeolites as means to recover entropic penalty around zeolite particles and to partially improve interfacial adhesion. Although such surface modification methods are beneficial to suppress the formation of interfacial voids, they require tedious time-consuming and multi-step procedures, typically resulting in low reproducibility. Instead, Adams et al. [11] demonstrated a substantial improvement of CO_2/CH_4 separation performance by fabricating polyvinyl acetate (PVAc)/zeolite 4A (50/50 vol/vol) MMMs without any surface modification of zeolites. A good adhesion between PVAc and zeolite 4A was achieved by simply inducing thermal relaxation of PVAc polymeric chains. Such polymers with low glass transition temperature, however, are avoided for gas separation application due to their poor mechanical stability and undesirable inherent transport properties.

Most previous studies associated with zeolite-containing MMMs have been performed based on a troublesome and tedious trial and error process [5]. In this study, we systematically demonstrated a theory-based fabrication of pristine MFI-type pure silica zeolite, silicalite-1, containing MMMs. For convenience' sake, silicalite-1 crystals are,

hereinafter, referred to as MFI particles. Lee et al. [15] proposed that the interfacial morphologies between MFI and polymer matrices could be determined by the adhesion force between them based on a simple Lewis acid-base interaction. Based on the van Oss and Good's Lifshitz-van der Waals acid-base theory, Lee's study provided a theoretical approach to estimate the relative extent of interactions between a series of polymer matrices and MFI crystallites based on the atomic force measurements [15]. It was demonstrated that the Lewis basicity of a polymer was the most critical parameter to determine the adhesion force between the polymer and MFI crystallites, where an increase in the adhesion force is associated with increasing acid (silanol groups on the surface of MFI)-base (basic groups in polymers) interactions, such as hydrogen-bonding. In an actual MMM fabrication, the interfacial morphology between polymers and molecular sieves, however, may be determined by many different factors including solvent-involved interactions (i.e., solvent-polymer and solvent-molecular sieve interactions), residual stresses, and film formation conditions [16]. Nevertheless, it is still informative to verify whether the simple theory based on the Lewis acid-base interaction provides a useful guide to selecting appropriate polymer matrices and thus, provide an insight into the successful fabrication of MMMs.

In this work, the compatibility between three different conventional polymer matrices (i.e., cellulose acetate (CA), polyimide (PI), and polysulfone (PSf)) and MFI particles was evaluated to demonstrate the feasibility of theory-based MMM fabrication method by performing morphology as well as transport characterizations. Especially, the gas transport behaviors of N_2 and NF_3 in CA/MFI MMMs were characterized by varying MFI particle sizes as well as their concentrations with the Lewis-Nielsen modeling-based predictions. Also, the effect of