Journal of Industrial and Engineering Chemistry 23 (2015) 238–242

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

CO_2/CH_4 separation through a novel commercializable three-phase PEBA/PEG/NaX nanocomposite membrane

A. Mahmoudi [a,b], M. Asghari [a,b,*], V. Zargar [a,b]

[a] Separation Processes Research Group (SPRG), Department of Engineering, University of Kashan, Kashan, Iran
[b] Energy Research Institute, University of Kashan, Ghotb-e-Ravandi Ave., Kashan, Iran

ARTICLE INFO

Article history:
Received 17 February 2014
Accepted 4 August 2014
Available online 23 August 2014

Keywords:
CO_2
Mixed matrix membrane
Zeolite X
Nanocomposite
PEBA

ABSTRACT

Three-phase polymer/liquid/solid (PEBA/PEG/nanozeolite X) mixed matrix membranes were synthesized. Effects of PEG and/or nanoparticle on CO_2 and CH_4 permeabilities and CO_2/CH_4 selectivity of the membranes were investigated. The synthesized membranes were characterized using AFM and SEM. CO_2 Permeability and selectivity in the membranes increased with feed pressure and PEG loading. The PEBA membrane with loadings of 30% PEG and 10% nanozeolite showed the best performance; its CO_2 permeability and CO_2/CH_4 selectivity at 8 bar were 95 Barrer and 45, respectively. Based on Robeson's upper bound, both the three-phase membranes of this work would be proper for being commercialized.

Introduction

Gas separation through polymer membranes is considered to be an effective tool for the separation of gaseous mixtures due to high separation efficiency, low running costs compared to conventional separation methods [1–3]. Attempts are being made to improve the performance by modifying the polymer both physically and chemically to bring about an increase in both flux and selectivity of the membrane. Literature reveals that physical modifications have been done through incorporation of fillers into the polymer matrix like zeolites, silica, alumina, carbon molecular sieves, and other inorganics [4–7]. Membrane gas separation is a dynamic and rapidly growing field due to the high selectivity and fluxes achievable by membranes, low energy requirements and easy to operate modules. Polymeric membranes have received the most attention in this field due to the manufacturability, low material costs, robust physical characteristics and good intrinsic transport properties. Polymeric membranes designed for gas separations have been known to have a trade-off between permeability and selectivity as shown in Robeson's upper bound curves. The transport of small molecules through a polymer membrane occurs due to random molecular motion of individual molecules [8]. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between the two phases [9]. At the present, polymeric membranes dominate the membrane separation field due to the fact that they are well developed and quite competitive in separation performance and economics [10]. One of the most interesting applications of the polymer membranes is the separation of CO_2 gas which is of significant importance in natural gas sweetening [11,12]. All liquid–polymer mixed matrix membranes have liquid polymer encapsulated in the continuous polymer matrix. The long-term stability of these membranes for industrial gas separation processes is still a critical issue because of the undesirable leakage of the liquid from the membrane. To stabilize the liquid in the polymeric membrane, a new type of MMMs, polymer–liquid–solid MMMs, has been developed most recently. The solid, such as activated carbon impregnated with liquid polymer such as poly ethylene glycol (PEG), functions as a stabilizer of the liquid polymer in the continuous polymer phase. These hybrid solid–liquid–polymer MMMs combine the properties of the continuous polymer phase, the dispersed solid filler phase, and the impregnated liquid phase [13–15]. Rahman et al. have prepared a Nano composite membranes by incorporation of commercial poly (ethyleneglycol) functionalized poly octahedral oligomeric silsesquioxanes (PEG-POSS) in PEBAX® MH 1657. They studied the effect of temperature upon CO_2 permeability and selectivity over N_2, O_2, CH_4 and H_2 between 30 °C to70 °C [16]. PEBAX® MH 1657/ZIF-7 mixed matrix

* Corresponding author at: Separation Processes Research Group (SPRG), Department of Engineering, Ghotb-e-ravandi Blv., Kashan, Iran.
Office: +983155912427; SPRG: +983155912823; fax: +983155912424.
E-mail address: asghari@kashanu.ac.ir (M. Asghari).

http://dx.doi.org/10.1016/j.jiec.2014.08.023
1226-086X/

Nomenclature

Abbreviations

AFM	atomic force microscope
DFV	dynamic free volume
EO	ethylene oxide
FFV	fractional free volume
MFM	mass flow meter
MMM	mixed matrix membrane
PA	polyamide
PEBA	poly(ether-block-amide)
PEG	poly (ethylene glycol)
PEO	poly(ethylene oxide)
SEM	scanning electron microscopy
XRD	x-ray diffractometery

Symbols

P_A	permeability of gas A
P_B	permeability of gas B
Δp_A	difference in partial pressure across the membrane
ℓ	membrane thickness
$\alpha_{A/B}$	selectivity
2θ	angle

membranes have prepared by Li et al. This hybrid material has been successfully deposited as a thin layer on a porous poly acrylonitrile (PAN) support. Both, permeability and CO_2/CH_4 gas selectivity increased at low ZIF-loading [17]. Poly(ether block amide) (PEBA) is a family of copolymers, consisting of polyamide hard segments and polyether soft segments in the polymer chains [18]. Because of their micro-biphasic structure, the copolymers offer many properties that are not readily available in either constituent polymer. PEBA not only has favorable membrane-forming properties but also good chemical resistance to acid, basic and organic solvents and high thermal and mechanical stabilities [19]. In this paper, PEBA 1657 copolymer, composed of 60 wt% of PEO and 40 wt% of PA6 (nylon-6) was used to prepare membranes [20]. This structure creates a blend of properties of thermoplastics and rubbers. The hard amide block provides the mechanical strength, whereas gas transport occurs primarily through the soft ether block [21,22]. Properties of PEBAX® MH 1657 are presented at Table 1 [23].

PEBAX® MH 1657 is soluble only in few solvents, formic acid, *n*-butanol and a mixture of 1-propanol/n-butanol. After cooling to room temperature these solutions show a strong tendency to gelation, which leads to difficult composite membrane preparation. To avoid gelation, formic acid can be used as a solvent, but use of formic acid for membrane preparation is inconvenient for large-scale membrane preparation. Surprisingly it was found that a simple binary mixture of ethanol/water (70/30 wt%) can easily dissolve PEBAX® and its blends with PEG. Dielectric constant for three types solvents are presented in Table 2 [24].

Poly ethylene glycol (PEG) (*MW* = 200), as a liquid polymer, is soluble in water and in many organic solvents, including aliphatic ketones and alcohols, chloroform, glycol ethers, esters, and aromatic hydrocarbons; they are insoluble in ether and in most aliphatic hydrocarbons; with increased molecular weight, ethylene oxide (EO) units in PEG polymer appear to be the most useful groups to achieve high CO_2 permeability and high CO_2/light gas selectivity. The difference in solubility is negligible for lower pressures at near the critical point of CO_2, but PEG with a higher *MW* at higher pressure could offer a reduced free volume to be occupied by the gas molecules. At the same time, the number of interactions between the end groups of the polymer chains and CO_2 molecules is higher for the polymer with lower *MW*, which account for the good solubility of CO_2 in PEG [25]. That was why we used PEG200 to improve the performance of PEBAX membrane. Characteristics of PEG200 are shown in Table 3.

To stabilizing the liquid polymer (PEG) in the continuous polymer phase, we used zeolite as filler. ZSM-5, mordenite, ferrierite and zeolite beta belong to channel group whereas zeolites A, NaX, NaY and Na-SZ18 are cage type zeolites having three-dimensional pore system. Cage-type structures demonstrate better performance than channel-type structure [26]. High adsorption capacity could be associated with the presence of supercages and sodalite cages that encapsulated adsorbates inside the structure [22,26–28]. Zeolite X with Si/Al Ratio 1.0–1.5 has Faujasite structure, three-dimensional pore structure formed by 12-member oxygen rings, large cavity of 13 Å and surrounded by 10 sodalite cages. 13X (NaX) zeolite show the best equilibrium performance at low feed and low regeneration of CO_2 pressures [22,25–29].

The purpose of this study was to prepare improved MMMs by the addition of PEG to the PEBA-NaX10% membranes for the gas separation process that it is expected that the permeability and selectivity would be improved.

Experimental

Materials

The materials and chemicals used for the membranes were PEBAX® (60 wt% PEO and 40 wt% of PA-6), nano zeolite X (SPRG) [27] and ethanol (Merck). PEG200 was purchased from LOBA Chemie. CO_2 and CH_4 gas cylinder with purity >99.999 were also applied.

Table 1
Properties of PEBAX MH® 1657 [23].

Mechanical properties	Dry/cond	Unit
Water absorption	120	%
Humidity absorption	4.5	%
Density	1140	kg/m^3
Glass transition temperature (10 °C/min)	40	°C
Melting temperature (10 °C/min)	204	°C

Table 2
Dielectric constant for different solvents [24].

Solvents	Dielectric constant
58.5 Formic acid	58.5
17.6 *n*-Butanol	17.6
Mixture ethanol/water (30/70)	45

Table 3
Properties PEG200 at 20 °C (Merck).

Characterized	Contents	Units
Vapor density	1>	(Compared to air)
Vapor pressure	0.01>	mmHg
Autoignition temperature	581	°F
Molecular weight	190–210	–
Viscosity	60	mPa s
Density	55 to 45	g/ml