Journal of Membrane Science 508 (2016) 136–145

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Poly(ether-*b*-amide)/ethylene glycol monophenyl ether gel membrane with superior CO_2/N_2 separation performance fabricated by thermally induced phase separation method

Chunfang Zhang, Yanyan Wu, Ying Zhang, Yunxiang Bai*, Jin Gu, Yuping Sun

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, PR China

ARTICLE INFO

Article history:
Received 19 November 2015
Received in revised form
11 February 2016
Accepted 13 February 2016
Available online 17 February 2016

Keywords:
Gel membrane
Pebax
CO_2 separation
Thermally induced phase separation

ABSTRACT

Polymeric gel membranes contain poly(ether-*b*-amide) (Pebax) and ethylene glycol monophenyl ether (EPH) was prepared via thermally induced phase separation (TIPS) method for the first time. In the membranes, EPH was used as not only diluent to form the gel structure, but also functional liquid to enhance the CO_2 permeability and CO_2/N_2 selectivity. Comprehensive investigation was carried out to study the phase separation behaviors and membrane performances. Phase diagrams and optical microscope results indicate that the crystallizition of Pebax from a one-phase solution is responsible for the physical network structure of the gel membranes. Meantime, the gel temperature shifted to the lower region with increasing EPH content. Both the pure CO_2 permeability and CO_2/N_2 ideal selectivity of the membranes were simultaneously increased with the increase of EPH content, which can be ascribed to the multiple synergistic effect of (a) the increased solubility of CO_2 by Lewis acid-base interactions between CO_2 and ethylene oxide groups in EPH, (b) the barrier effect of EPH on the transport of N_2 and (c) more permeable amorphous phase was formed in polymer matrix. The overall performance of gel membranes with 60 and 80 wt% EPH fall within the attractive region beyond the "Robeson Upper Bound" for CO_2/N_2 gas pairs. The successful application of TIPS provides a new route to the structure modulation and performance enhancement of polymer gel membranes in the removal of CO_2 from gas streams.

1. Introduction

Carbon dioxide capture from power plant flue gas and subsequent sequestration is expected to play a key role in mitigating global climate change. Membrane separation is one of the most potential methods to remove CO_2 from flue gas [1,2]. Compared with other separation methods, such as adsorption and cryogenic separation, membrane separation is being recognized to have the advantages of low energy consumption, mechanical simplicity, ease to scale up and smaller footprint and so on [3]. Nowadays, the membranes for CO_2 separation can be classified as polymeric membranes, inorganic membranes, mixed matrix membranes and supported liquid membranes. Most polymeric membranes are cost effective and easy processing. But they are apt to be damaged at high temperature and corrosive conditions [4]. Additionally, the tradeoff between permeability and selectivity is one of the biggest problems that polymeric membranes faced with [5]. Inorganic membranes offer much higher permeabilities than polymeric membranes and also high selectivities in many separations of technological interest. However, challenging issues in inorganic membranes, such as reproducibility of membrane manufacture and control over defect formation must be overcome to realize industrial applications [6]. Mixed matrix membranes can combine the merits of easy processing of polymer membranes and superior permeability and selectivity of inorganic membranes [7]. But their separation performances are prone to deteriorate due to the fact that there are inevitably non-selective voids generating at the interface of polymer and inorganic particles [8]. Supported liquid membranes have both satisfied selectivity and high permeability. Unfortunately, they are inadvisable to be used at high temperatures and cross-membrane pressures, which is the main obstacle to their further application in industry [9].

In recent years, polymer gel membrane has emerged as a new membrane material in CO_2 separation process. One of the most striking features of polymer gel is that a large amount of "functional liquid" is enwrapped in a tangled network created by chemically or physically crosslinked polymers or long-chain molecules. The liquid can obstruct the polymer chains from collapsing into a compact mass; while the network can hold the liquid from flowing away. As a form of matter between solid and liquid, the

* Corresponding author.
E-mail address: baisir223@163.com (Y. Bai).

http://dx.doi.org/10.1016/j.memsci.2016.02.030
0376-7388/

polymer gel membrane tend to have liquid-like transport properties for better diffusivity and thus better separation productivity (i.e., through-put) [10]. Besides, most functional liquid tend to possess the properties of good affinity with CO_2, resulting in a high selectivity of the gel membrane, simultaneously. Although both a gel membrane and a supported liquid membrane are constructed by physical interactions between the polymer chains and the functional liquid, they do have different microstructures. In gel membranes, the microstructure may be more homogeneous because the polymer chains is dissolved before the phase separation occurs according to the fabricating process of a gel membrane. While, in supported liquid membranes, the functional liquid is just trapped in the pores of polymer porous membrane via capillary force. So a gel membrane would be more stable than the supported liquid membranes.The gel membranes can also solve the problem of incompatibility of the mixed matrix membranes, because the non-volatile functional liquid has better compatibility with polymer than inorganic particles. In the past few years, most research works have been presented on the preparation of gel membrane for gas separation. Friess et al. prepared ionic liquid polymeric gel membranes using 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide ([EMIM][TFSI]) as the functional liquid and poly(vinylidene fluorideco-hexafluoropropylene) (p (VDF-HFP)) as polymer matrix. Gas permeation measurements showed a significant increase of permeability in the presence of [EMIM][TFSI], especially for CO_2 [11]. Rabiee et al. investigated separation performance of poly(ether-*b*-amide 6) (Pebax1657)/glycerol triacetate (GTA) gel membranes for CO_2 removal from N_2 [12]. The overall performance of membranes for CO_2/N_2 separation was improved to the upper bound of Robeson graph. Recently, another polymeric gel membranes with hydrocarbon surfactants Tween as the functional liquid were prepared by Dong et al. using a solvent evaporation method [13]. The best separation performance, CO_2 permeability of 289 Barrer and CO_2/N_2 selectivity of 40.70 at 0.6 atm and 25 °C, was achieved for the Pebax2533/Tween80 gel membrane.

Up to present, gel membranes were mainly prepared by solvent evaporation (SE) method, in which a suitable and volatile co-solvent is chosen to blend a polymer and a functional liquid uniformly. Upon evaporation of the co-solvent, phase separation occurs and a continuous physically crosslinked gel extending throughout the volume of the system will be formed. The drawback of the method of SE is that a large amount of solvent would be wasted in the process of membrane preparation, causing environmental pollution consequently. More importantly, the solvent evaporation speed is difficult to be precisely controlled which is vital to achieve a foreseeable membrane structure.

Quenching polymer solution for gelation (thermally induced phase separation) and swelling of a neat polymer film in functional liquid are alternative ways to prepare polymer gel membrane [14].These two methods are generally “green” procedures without solvent evaporation. However, the swelling method is not suitable to obtain high functional liquid concentrations because the membrane is easily deformed or damaged during the swelling. Thermally induced phase separation (TIPS) is a well-known method to fabricate polymer gel and porous separation membranes due to its advantages including easy control, low tendency for defects formation and diverse microstructures. Since it had been introduced by Castro in 1980 s, this method has attracted wide investigations in respect of conducting process, phase separation mechanism, structure controlling and properties enhancement [15–18]. In a typical TIPS process, a polymer is dissolved in a diluent at high temperature. Then the homogeneous polymer solution is cooled down to induce the phase separation and form the gel network consequently. The so-called diluent also acts as the functional liquid for a polymer gel membrane during CO_2 separation process. On the other hand, if the diluent is removed by solvent extraction, a microporous structure would be produced, which leads to a porous membrane [19–23]. Numerous works have been presented on the porous membrane preparation by the TIPS process. However, to the best of our knowledge, no systematic study on the preparation of polymer gel membrane by the TIPS has been reported for gas separation process.

Herein, we successfully prepared poly(ether-*b*-amide) (Pebax)/Ethylene glycol monophenyl ether (EPH) gel membranes by the method of TIPS. Pebax has excellent mechanical properties and crystalline/amorphous structure, where the polyamide segment is insoluble and the polyether segment is soluble in EPH. Such a physically cross-linked gel only requires a few weight percent of polymer to achieve polymeric gel membrane with high EPH content. Furthermore, the mechanical properties of the gel membrane can be tuned by varying ether and amide compositions [24–26]. Ethylene glycol monophenyl ether (EPH) were selected as functional liquid, since there are many ethoxy group in EPH's molecular structure, which is widely accepted to has strong affinity to CO_2 [27]. Moreover, the electrophilic of benzene ring endows ethoxy group much stronger polarity which is helpful to adsorb CO_2. In this paper, different characterization techniques have been applied to gain insight into the thermal, mechanical and structural properties of the gel membranes prepared by varying EPH content, and their correlation with the transport properties were analysed, in view of the potential use of such membrane in CO_2 recovery and purification.

2. Experimental

2.1. Materials

Pebax (grade 4033), containing 53 wt% poly(tetramethylene oxide) (PTMO) and 47 wt% Nylon-12 (PA), was supplied from Arkema Inc., France, in the form of elliptic pellets. EPH was purchased from National Pharmaceutical Group Chemical Reagent Co. Ltd, China. Some of the main characteristics of Pebax and EPH introduced with the supplier are presented in Table 1. CO_2 and N_2 were supplied by Wuxi Xinnan Chemical Gas Co. Ltd., China, and were of at least 99.99% purity. All the purchased chemical materials were used as received without further treatment.

2.2. Preparation of Pebax/EPH blend samples

Pebax and different amounts of EPH were added into a flask, heating at 180 °C and stirring for at least 4 h under the protection of nitrogen until a clear homogeneous solution was obtained. The solutions were quenched by liquid nitrogen to gain the solid Pebax/EPH blend samples.

2.3. Determination of phase diagram

Gelation temperature (T_{gel}) was measured as follows [30]. The solid Pebax /EPH blend samples in a test tube was heated to 180 °C to be melted. Then, the solution was quenched at a constant temperature. After standing for 24 h, the test tube was inverted. The temperature at which the solution no longer flew was the gel temperature of the Pebax /EPH system.

Dynamic crystallization temperature (T_c) was determined by a differential scanning calorimeter (Mettler DSC 7, Switzerland). The solid sample was sealed in an aluminum DSC pan, melted at 180 °C for 3 min, and then cooled at 10 °C/min to 25 °C. The onset of the exothermic peak during the cooling was taken as T_c.

Optical microscopy observation was measured according to the method reported by Matsuyama et al. [31]. In detail, a certain