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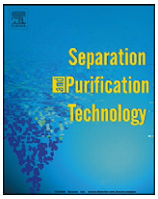

Study of gas separation properties of ethylene vinyl acetate (EVA) copolymer membranes prepared via phase inversion method

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ABSTRACT

The gas separation properties of ethylene vinyl acetate (EVA) membranes containing 18 and 28 wt% of vinyl acetate (VA) were investigated in this study. The effects of membrane preparation conditions, such as thermal and thermal/wet phase inversion, and the type of solvent on the gas separation properties of EVA membranes were investigated. The permeation of pure O_2, N_2, CH_4, and CO_2 gases at different feed pressures ranging from 2 to 11 bar were examined.

The results indicated that the CO_2 permeability was evidently higher than those of the other gases. Furthermore, the solubility mechanism was found to be the dominant mechanism for permeation of gases through EVA membranes. Moreover, the membranes prepared using tetrahydrofuran (THF) as solvent showed higher gas permeabilities than those prepared using chloroform ($CHCl_3$) as solvent.

The results indicated that the gas permeabilities through membranes prepared using wet phase inversion technique were higher. Also, the membranes prepared by thermal/wet phase inversion method at higher temperatures showed improved gas separation properties. In addition, the membrane with higher VA content prepared using THF as solvent presents higher gas separation properties. Trade-off evaluation also showed that certain types of the prepared EVA membranes in this study have potential for commercialization.

1. Introduction

During the past few decades, membrane technology for gas separation has emerged as a viable alternative to conventional technologies such as cryogenics, catalytic, and pressure swing adsorption. An important factor in making a membrane process economically feasible is to fabricate membranes with high permeability, high selectivity, and high mechanical and thermal stability [1]. Over the past decades, application of polymeric membranes in gas separation has steadily grown, encouraging the research communities to attempt to develop polymeric membranes with enhanced performance for gas separation applications. In particular, more attention has been given to the studies focused on the improvement of quality of both glassy and rubbery polymers for gas separation. Among available polymers, aromatic polysulfones [2,3], polycarbonates [4,5], polyarylates [6,7], polyaryl ketones [8], polyarylene ethers [9] and polyimides [10–14] have demonstrated appropriate potential for gas separation. In recent years, some of these polymers, such as polycarbonates, polysulfones, polyimides, polyetherimides and poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) have been commercialized. Meanwhile, many researchers tried to prepare novel gas separation membranes from various types of polymers [15–17]. These research activities were aimed at two main goals: (i) improving gas separation properties of membranes by changing chemical composition of membranes and (ii) improving gas separation properties of membranes by effectively controlling membrane preparation conditions. While the first goal can be achieved by adding new bulky, electronegative or polar groups into the macromolecules, the second goal needs properly choosing solvents and effectively controlling the solvent extraction steps.

It is well understood that the final properties of the prepared membranes are greatly affected by the selected preparation method. Among different methods of membrane preparation, the phase inversion technique has received more attention. This technique can be applied for the preparation of polymeric membranes in different ways: dry phase inversion, wet phase inversion and thermal phase inversion [1]. Because the final characteristics of the membranes prepared by the above methods differ considerably, the

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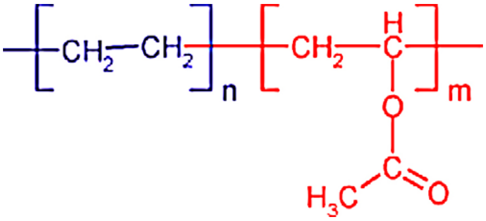

Fig. 1. Chemical structure of EVA copolymer.

most proper method has to be carefully chosen for the preparation of a certain membrane.

In recent years, ethylene vinyl acetate (EVA) copolymer has been used for membrane preparation in various applications. Marais et al. [18,19] studied the O_2, CO_2 and H_2O permeabilities of EVA copolymer and its blends with PVC using the dry phase inversion method and dichloromethane as solvent. Marais et al. showed that the H_2O/CO_2 and H_2O/O_2 selectivities increase by an increase in the vinyl acetate (VA) content of the copolymer.

Separation of CO_2 gas from CO_2/N_2 gas mixtures (known as off-gas) is one of the main concerns of the industry. CO_2 is a polar gas with good affinity to polar groups of polymers. Therefore, polymers and copolymers such as polyvinyl acetate (PVAc) seemed to be good candidates for membrane preparation to separate CO_2 from off-gases.

Although PVAc has polar acetate groups in its structure, its low mechanical strength prohibits its application as a gas separation membrane. On the other hand, EVA copolymer has adequate mechanical stability and flexibility for fabrication of CO_2/N_2 separation membranes due to the presence of polar carbonyl groups with polyethylene groups in its structure. The chemical structure of EVA is given in Fig. 1.

The authors have previously published [20,21] their investigations on casting different films of EVA by thermal and thermal/wet phase inversion methods and investigated the effects of different preparation conditions including the coagulation bath temperature, polymer solution composition, preliminary drying time, and thickness of the cast film on the morphology of EVA films. Based on the morphological behaviors of the cast films under different preparation conditions, it was concluded that some of the membranes developed dense layers are suitable for gas separation applications. Presently, not much data is available on the effects of the preparation conditions of EVA membranes on its gas separation properties. Therefore, the objectives of the present study were: (i) to investigate the effects of the preparation and operational conditions on the gas separation properties of the final membrane and (ii) to find the suitable conditions under which the reasonable gas permeability and selectivity are achieved.

In the light of the above discussion, EVA copolymers with different VA content were selected for preparation of CO_2/N_2 separation membranes. Also, because type and particularly volatility of solvents influence the properties of the membranes, two different solvents, namely, THF and $CHCl_3$, were used to prepare the casting solutions from EVA copolymers. Thermal and wet phase inversion methods were also applied to prepare the membranes. The effects of the preparation conditions and the chemical structure of the polymer on the permeabilities of pure O_2, N_2, CH_4, and CO_2 gases through the prepared membranes were investigated.

2. Experimental

2.1. Materials

Tetrahydrofurane (THF) and chloroform ($CHCl_3$) solvents were purchased from Merck Company. EVA copolymers containing 18 and 28 wt% of VA, hereafter called EVA-18 and EVA-28, respectively, were provided by Exxon Chemical (Belgium) and Asia Polymer Corporation (Taiwan).

Distilled water was used as precipitant and O_2, N_2, and CO_2 gases with 99.99% purity (Roham Gas Corp., Tehran, Iran) and ultra high purity CH_4 gas (Air Products Co.) were used in permeation experiments.

2.2. Membrane preparation method

Thermal and thermal/wet phase inversion techniques were applied for preparation of EVA membranes. In thermal phase inversion method, EVA copolymers were dissolved in THF or $CHCl_3$ at 60 °C. To prevent excessive solvent vaporization, a reflux stream was used to prepare 6.5 wt% of EVA/solvent solution. The EVA/solvent solution was cast on a glass plate using a doctor blade at room temperature. The casting was done as quickly as possible to obtain uniform films. The glass plate was immersed in distilled water at room temperature to detach it from the plate.

In the thermal/wet phase inversion method, solution of 12 wt% EVA in THF was cast on a glass plate and then transferred to a coagulation bath after 10 s of solvent evaporation. The temperature of the coagulation bath was set at 20, 40 and 55 °C. Phase inversion started immediately after the immersion of the cast films, and thin polymeric films detached from the glass plates after a few minutes. After about 20 minutes, when the solvent extraction was almost completed, the film was air dried at room temperature. Table 1 shows the preparation conditions of EVA membranes.

2.3. Gas permeation tests

Nitrogen, oxygen, methane, and carbon dioxide permeabilities of the prepared membranes were determined using a constant pressure/variable volume method at room temperature (25 °C). The gas permeation setup has been described elsewhere [22]. The feed pressure was 2, 4, 6 and 8 bar. The permeates were collected at atmospheric pressure. The gas permeability was determined from the following equation:

$$P = \frac{ql}{\Delta pA} \quad (1)$$

Table 1
The preparation conditions of EVA membranes

Sample name	Polymer	Phase inversion technique	Solvent	Coagulation bath temperature
Wet-55	EVA-28	Thermal/Wet	THF	55 °C
Wet-40	EVA-28	Thermal/Wet	THF	40 °C
Wet-20	EVA-28	Thermal/Wet	THF	20 °C
THF-28	EVA-28	Thermal	THF	Room temperature
THF-18	EVA-18	Thermal	THF	Room temperature
CL-28	EVA-28	Thermal	$CHCl_3$	Room temperature
CL-18	EVA-18	Thermal	$CHCl_3$	Room temperature