

Pebax[®]/polyethylene glycol blend thin film composite membranes for CO₂ separation: Performance with mixed gases

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Received 26 October 2007; received in revised form 2 January 2008; accepted 3 January 2008

Abstract

The paper describes the performance of Pebax[®]/polyethylene glycol (PEG) blend thin film composite membranes for CO₂ separation from gas mixtures containing H₂, N₂ and CH₄. Membranes were tested at different conditions; temperature and pressure dependence of gas flux and selectivity were explored. The temperature dependence was correlated with the Arrhenius equation to determine the activation energy of single gas permeation. Single and mixed gas permeation was measured for different pressures at 293 K up to 20 bar. Improved permeabilities and CO₂/H₂ selectivities were obtained in the newly developed composite membranes.

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Keywords: Pebax[®]; Thin film composite membranes; CO₂ separation; Mixed gases

1. Introduction

Today's industrial production and infrastructure in the world are based on fossil fuel use [1], which is related directly with the generation of energy. Thus, it is believed that the combustion of fossil fuels and other human activities are the reasons for the increased concentration of greenhouse gases all over the world [2], where carbon dioxide (CO₂) is one of the largest contributors to global warming. Therefore, its capture from different sources such as power stations, oil refineries and large cement works is very important. Flue gas usually contains low concentration of CO₂ (<20%); typical CO₂ concentrations in process streams are shown in Table 1 [3].

Another separation problem is the presence of CO₂ in natural gas, where it causes reduction of the heating value and waste of pipeline capacity [4]. For its removal, a wide variety of technologies are available, including especially chemical and physical

absorption processes; each process has its own advantages and disadvantages [5]. Currently, membrane processes are considered as promising technology within the trains for treating gas streams. Advantage of membrane technology is its simplicity, i.e. no absorbent, which has to be regenerated; it can be easily retrofitted, modularized and scaled-up for several applications [6].

Despite the early acceptance of polymeric membranes for gas separation, no large-scale applications were introduced until the seventies of last century [7]. Main reason was the lack of polymeric membrane materials and membrane structures, which could combine high selectivity and high flux. Commercial membrane systems for gas separation were available since the mid-1970s, but the most important innovation for large-scale commercialization of polymeric membranes for gas separation was achieved by Permea (now Air Products) in 1980 [8]. This success of commercialization of polymeric membranes increased the investigations related to the development of new membrane materials and techniques of membrane preparation, and since then, many applications for membrane-based gas separation have been developed (see Table 2) [9].

The permeation properties of a polymeric membrane depend on the chemical microstructure, crystallinity and morphology of the polymer [10]. Permeant properties like size, shape and polarity determine transport properties [11]. The permeability depends on the solubility and diffusion coefficient of the per-

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Table 1
Typical CO₂ concentration in process streams

Process	CO ₂ concentration (vol.%)
Power plant flue gas	
Coal fire boiler	14
Natural gas fire boiler	8
Natural gas combined cycle	4
Coal–oxygen combustion	>80
Natural gas partial oxidation fuel gas	40
Blast furnace gas	
Before combustion	20
After combustion	27
Cement kiln off-gas	14–33
Oil refineries and petrochemical plant fired heater	8

meant species in the polymer. Generally, better selectivities are obtained with glassy polymers because the diffusion coefficients in this type of material are more dependent on molecular size than in rubbery polymers [12]. Typical glassy polymers used in membranes for commercial gas separation, are polysulfone, cellulose acetate and polyimides [13]. Membranes prepared from rubbery polymers can be found in commercial applications as well, for instance silicon membranes are used for organic vapor separation and oxygen enrichment [14].

Membrane materials with high separation performance, i.e. high flux and high selectivity, are crucial for industrial application; in addition, large-scale composite membrane preparation must be feasible and simple. An important factor is the use of environmental-friendly solvents during the membrane preparation.

It was shown that polyamide–polyether (Pebax®) block copolymers could fulfil the above-mentioned requirements especially due to their good selectivity for carbon dioxide over hydrogen and nitrogen [15–19]. In a recent paper we reported

an improved and advantageous method to prepare homogeneous Pebax films by using a mixture of ethanol and water at room temperature [20]. The use of this binary solvent and the addition of polyethylene glycol allowed the preparation of films with improved properties; these results led us to develop multicomponent thin film composite membranes.

In this work we compile the performance of Pebax®/PEG blend thin film composite membrane at different temperatures and pressures; single gases and mixtures of CO₂/H₂, CO₂/N₂ and CO₂/CH₄ up to 20 bar were investigated. Obtained results give us a guideline for future scale-up and the commercial applications for Pebax®/PEG blend membranes.

2. Experimental

2.1. Materials and membrane preparation

Pebax® MH 1657 (Arkema), PEG 200 (Aldrich) and ethanol (Aldrich) were used without further purification. A mixture of ethanol/water (70/30 wt.%) was used as solvent to prepare the polymer solution (3 wt.% of Pebax®) under reflux at 80 °C for 2 h (stirred). After cooling down the solution to room temperature, different amounts of PEG 200 (molecular weight of 200 g/mol) were added and stirred again for 1 h. The ethanol/water mixture is a binary solvent which does not cause gelation of the polymer solution at room temperature and it also does not damage the membrane used as support. Transparent and homogenous polymer-casting solutions were filtered before composite membrane preparation. PAN HV (III) (polyacrylonitrile) microporous support membrane manufactured by GKSS was firstly coated with a dilute polymer solution (0.5 wt.% of Pebax® in ethanol/water binary solvent) in order to prevent the extraction of PEG 200 into the microporous structure of PAN support. The coated support was then dipped into the 3 wt.% solution of Pebax with different PEG content. After the dip-

Table 2
Gas membrane application and suppliers

Gas separation	Application	Supplier
O ₂ /N ₂	Nitrogen generation Oxygen enrichment	Permea (Air Product) Generon (IGS), IMS (Praxair), Medal, Parker gas separation
H ₂ /hydrocarbons	Refinery hydrogen recovery	Air Products, Air Liquide, Praxair
H ₂ /CO	Syngas ratio adjustment	As above
H ₂ /N ₂	Ammonia purge gas	As above
CO ₂ /CH ₄	Acid gas treating Enhanced oil recovery Landfill gas upgrading	Cynara (NATCO) Kvaerner, Air Products Ube
H ₂ S/hydrocarbon	Sour gas treating	As above
H ₂ O/hydrocarbon	Natural gas dehydration	Kvaerner, Air Products
H ₂ O/air	Air dehydration	Air Products, Parker Balston, Ultratroc, Praxair
Hydrocarbons/air	Pollution control Hydrocarbon recovery	Borsig, MTR, GMT NKK
Hydrocarbons from process stream	Organic solvent recovery Monomer recovery	MTR, SIHI, GMT

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