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PEG modified poly(amide-*b*-ethylene oxide) membranes for CO_2 separation

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Abstract

In the present work, membranes from commercially available Pebax® MH 1657 and its blends with low molecular weight poly(ethylene glycol) PEG were prepared by using a simple binary solvent (ethanol/water). Dense film membranes show excellent compatibility with PEG system up to 50 wt.% of content. Gas transport properties have been determined for four gases (H_2, N_2, CH_4, CO_2) and the obtained permeabilities were correlated with polymer properties and morphology of the membranes. The permeability of CO_2 in Pebax®/PEG membrane (50 wt.% of PEG) was increased two fold regarding to the pristine Pebax®. Although CO_2/N_2 and CO_2/CH_4 selectivity remained constant, an enhancement of CO_2/H_2 selectivity (∼11) was observed. These results were attributed to the presence of EO units which increases CO_2 permeability, and to a probable increase of fractional free-volume. Furthermore, for free-volume discussion and permeability of gases, additive and Maxwell models were used.

Keywords: Pebax®; Blend membranes; Gas separation; Carbon dioxide

1. Introduction

Carbon dioxide (CO_2) has been identified as the major greenhouse gas responsible for global warming. The energy industries, industrial combustion of fossil fuel, transport and construction are the largest contributors for CO_2 emission. By Kyoto protocol or United Nations Framework Convention on Climate Change (UNFCCC), the emission targets of the greenhouse gases have to be reduced by 8% until the end of 2012 [1]. This target covers emissions of the six main gases, namely carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride. CO_2 (an acid gas) is found in flue and natural gas stream and for its removal many conventional technologies are available, where absorption and cryogenic processes are mainly known [2–4]. However, the development of new, innovative and flexible mechanisms to reduce emissions of this gas are very important in the industrial processes. Membrane separation is an emerging technology for CO_2 capture. Membrane processes are preferred in small and medium scale separations and when product purity requirements are not extremely stringent [5].

During the last two decades, many new polymers have been developed for gas separation membranes which have been described in literature [6–10]. Recently, Lin and Freeman [11] have reported an overview about material selection for membrane preparation that remove CO_2 from gas mixtures. In that article, CO_2 solubility and CO_2/gas solubility selectivity in solvents and polymers containing different polar groups were discussed. They have concluded that ethylene oxide (EO) units in the polymer appear to be the most useful groups to achieve high CO_2 permeability and high CO_2/light gas selectivity. Homopoly(ethylene oxide) (PEO) consists of EO monomeric units, but its disadvantage is the strong tendency to crystallize and consequently it presents low gas permeability [12]. Block copolymers containing EO units as poly(amide-*b*-ether) has been shown as alternative material for this purpose. These copolymers were developed in 1972 but in 1981 began to be used for commercial purpose under the trade name Pebax® produced by ATOCHEM [13] (now ARKEMA). Pebax® is a thermoplastic elastomer having the following general chemical structure (Scheme 1): PA is

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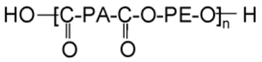

$$\mathrm{HO}-\!\left[\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\text{-PA-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\text{-O-PE-O}\right]_n\!-\mathrm{H}$$

Scheme 1. Chemical structure of Pebax®.

an aliphatic polyamide “hard” block (e.g., nylon-6, nylon-12) and PE is an amorphous polyether (polyethylene oxide (PEO) or polytetramethylene oxide (PTMO)) “soft” block [14]. The PA blocks provide the mechanical strength and gas transport occurs through the PEO phase [15]. Block copolymers with immiscible soft and rigid blocks like Pebax® can form various microphase-separated structures [16]. Varying the polyamide and polyether segment, molecular weight and the content of each block, the mechanical, chemical, and physical properties can be conventionally modeled [17].

Pebax® has been shown as promising membrane materials for acid gas treatment [18–21]. Bondar et al. [18] have studied CO_2/N_2 and CO_2/H_2 separation using different grade of Pebax® membranes. They have reported high CO_2/N_2 and CO_2/H_2 selectivity, which were attributed to high CO_2 solubility due to the strong affinity of the polar ether linkages for CO_2. Kim et al. [19] have also reported high permeability and high selectivity for CO_2 over N_2 as well as SO_2 over N_2, and these properties were attributed to polarizability of gases due to PEO segments. On the other hand, mesoblends of polyether block copolymers and poly(ethylene glycol) (PEG) were generated by Patel and Spontak [22], and it was found that CO_2/H_2 selectivity can be improved by incorporation of PEG. The effect of PEG in the polymer chain to CO_2 transport properties in different polymer systems was also described by other researchers [23–27] and it was proven that EO units influence CO_2 transport in glassy and rubbery polymers.

In this work we present Pebax®/PEG blend membranes with improved properties in respect to pristine poly(amide-*b*-ether) block copolymer. It was expected that incorporation of PEG into the Pebax® matrix would lead to membranes with improved performance for CO_2 separation. This is analog to the old work of Kulprathipanja [28], who dispersed PEO in PDMS and improved the permeability for CO_2. In addition, we also present an advantageous method to prepare membranes with enhanced properties by using a simple binary solvent (ethanol/water).

2. Experimental

2.1. Materials and membrane preparation

Pebax® MH 1657 (Arkema) (comprise 60 wt.% of PEO and 40% PA-6), PEG200 (Aldrich) and ethanol (Aldrich) were used without further purification. A mixture of ethanol/water (70/30 wt.%) was used as solvent to prepare polymer solution (3 wt.% of Pebax®) under reflux at 80 °C and 2 h stirring. After cooling down the solution to room temperature, different amounts of PEG200 (molecular weight of 200 g/mol) were added and stirred for 1 h. The obtained homogeneous solution was filtered trough a steel filter with pore size 32 μm (F. Carl Schröter, Hamburg, Germany) and poured into an aluminium ring supported by a flat glass plate. Subsequently, solvent evaporation was controlled by covering it with a glass dish for 48 h at 30 °C. The obtained membranes were dried in a vacuum oven overnight at 30 °C to remove residual solvent. By optical observation all samples showed an excellent miscibility between Pebax® and PEG. Membrane thickness measured by a digital micrometer (Deltascope® MP2C) varied from 60 to 100 μm. Densities of membranes were determined by buoyancy method in a perfluorinated liquid (3M Fluorinert™ FC-77) with known density (1.766 g/cm^3).

2.2. Membrane characterization

Thermal properties of samples were characterized in the temperature range from −100 to 250 °C by using a Netzsch (Differential Scanning Calorimetry) DSC 204 calorimeter. Measurements, including baseline determinations were performed at the scan rate of 20 K/min, and the experiments were conducted by using a nitrogen purge gas stream. Melting and glass transition temperature values were obtained from first scan thermograms.

Permeabilities of four pure gases (hydrogen, nitrogen, methane and carbon dioxide) were measured by a pressure increase time-lag apparatus at 30 °C [29], where the feed pressure was 600×10^2 Pa (600 mbar) for all gases.

The resulting morphology of membranes was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM analyses were carried out with LEO 1550 VP Gemini (ZEISS) equipment, and AFM was conduced by a Veeco Multimode in tapping mode at room temperature.

3. Results and discussion

3.1. Membrane preparation and thermal properties

Pebax® copolymers are hydrophilic and they show excellent chemical resistance towards solvents. The solubility of these copolymers in different solvents is determined by the ratio of PA and PEO blocks. Higher content of PEO makes the polymer more hydrophilic and thus, it leads to different solubility property [19,30]. Pebax® MH 1657 is soluble only in few solvents, formic acid, *n*-butanol and a mixture of 1-propanol/*n*-butanol. [20]. Usually, the solution is prepared under reflux at high temperature and low concentration using *n*-butanol or a mixture *n*-butanol/1-propanol; 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 [31] that a simple binary mixture of ethanol/water (70/30 wt.%) can easily dissolve Pebax® and its blends with PEG. Advantage of this solvent is the stability of the polymer solution at room temperature, which simplifies the membrane preparation process. The solubility parameter (δ) for Pebax® MH 1657 estimated by Small method was found as 22 MPa$^{0.5}$ approximately [32,33]. Thus solvents or mixtures of two or more solvents which have a sol-