



Mixed matrix membranes composed of various polymer matrices and magnetic powder for air separation



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ABSTRACT

Ethylcellulose (EC), linear polyimide (LPI) or hyperbranched polyimide (HBPI) and magnetic neodymium powder MQP-14-12 have been used for the preparation of magnetic mixed matrix membranes (MMMs). Permeability diffusion and sorption coefficients of O₂, N₂ and synthetic air components were estimated for homogeneous and heterogeneous membranes using the time lag method based on dynamic experiments in a constant pressure system. The effect of magnetic powder particles on the gas transport properties of MMMs was studied. The results showed that the membrane permeation properties were improved with the magnetic neodymium particle filling. It was observed that the magnetic ethylcellulose and polyimide membranes showed higher gas permeability, while their permselectivity and solubility were rather maintained or slightly increased. The results also showed that the magnetic powder addition enhanced significantly gas diffusivity in EC and polyimide membranes.

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1. Introduction

Over the past few decades, membrane separation process was found to be promising for various medical and industrial applications (air separation, hydrogen recovery and CO₂ removal) [1–7]. Membrane technology is an attractive separation approach due to such advantages offered by the process, like: high stability and efficiency, ease of operation, low operating cost and energy requirement [8–10]. The major issue of current membrane research is developing of highly permeable and selective membrane materials, that also show sufficient resistance [11]. Because of that the development of new polymers or the modification of existing polymers for gas separation is a very important factor [12,13]. These polymers can be easily modified by various substitutions and insertion of the metal cations, like: Na⁺, Mg²⁺, Al³⁺, a production of copolymers or carbon membranes received by pyrolysis of polymer precursors [14–17]. The next, very promising strategy for improving the mass transport through polymer films is the incorporation of inorganic materials (zeolites, carbon molecular sieve, silica nanoparticles, etc.) into a polymer matrix. This new class of membrane materials, that offers the significant potential in membrane separation technology is called mixed matrix

membranes (MMMs). These membranes combine the selectivity of fillers and the simplicity of polymer membrane processing [18]. The successful application of MMMs depends mainly on the polymer matrix selection, the inorganic filler as well as the interaction between these two phases [19–27]. Recently, much attention has been devoted to usage of aromatic polyimides (PIs) as the polymer matrices, especially because of their high selectivity in gas separation and their excellent thermal, chemical and mechanical stability [28–33].

Based on shown above information, it could be seen that the air separation using the polymer membranes is a significant challenge. The next solution of this problem would be to provide differentiated conditions (other than sorption–diffusion) in mass transport between the oxygen and the nitrogen. These necessary differences were delivered by the presence of magnetic field, which actively influences the oxygen and nitrogen transport. This difference in magnetic properties of oxygen (paramagnetic) and nitrogen (diamagnetic) was, until now, used only in magneto-responsive colloidal systems [32–34].

Over the past few years, our group has performed extensive research on the polymer membranes prepared from ethyl cellulose and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) filled with neodymium powder or iron oxides. Such membranes have been used to the oxygen air enrichment [35–37,40]. This paper is the continuation of our earlier work, where we have found that incorporation

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of magnetic powder MQP-0 (20–32 μm and 32–50 μm) improved the transport properties of EC and PPO membranes. Now we are going to use another type of magnetic powder MQP-14-12 with granulation 25 μm and different polymer matrices (LPI and HBPI) which are known as very selective and stable. Transport properties of the obtained membranes were analysed using a constant pressure permeation technique. The impact of the magnetic particle content in various polymer matrices on the transport and separation properties of investigated membranes in the gas mixture (O_2/N_2) separation processes was analysed.

2. Experimental

2.1. Materials

Ethylcellulose (EC) was supplied by Acros Organics. 4,4'-oxydiphthalic anhydride (ODPA) (Chriskev, USA) was heated to 180 °C overnight in a vacuum before use. 4,4'-methylenedianiline (MDA) (Aldrich, Czech Republic) and 4,4',4''-triaminotriphenylmethane (MTA) (Dayang, China) were used as received. *N*-methylpyrrolidone (NMP) (Merck, Czech Republic) was distilled in a vacuum over phosphorus pentoxide and stored in an inert atmosphere. The neodymium magnetic powder MQP-14-12 was used as an inorganic filler. The magnetic powder MQP-14-12 with 25 μm granulation is a product of Magnequench company. Ethanol, toluene and trichloroethylene (TCE) with 99% purities were supplied by Sigma Aldrich. Oxygen, nitrogen and synthetic air compressed cylinders were supplied by Linde Gas.

2.2. Membrane preparation

In our research, we have examined the homogeneous ethylcellulose (EC), LPI (linear polyimide), HBPI (hyperbranched polyimide) and heterogeneous magnetic membranes of thickness 90–250 μm (depending on the amount of added magnetic powder). The hyperbranched polyamic acid (HBPA) and linear polyamic acid (LPAA) were prepared in a two necked flask equipped with a magnetic stirrer and a nitrogen inlet/outlet. At room temperature, a 4 wt% ODPA solution in NMP was added dropwise to a 4 wt% solution of MTA or MDA in NMP (ODPA/MTA and ODPA/MDA molar ratios were 1:1). This reaction mixture was then stirred at room temperature for 24 h. A solution of either HBPA or LPAA in NMP was cast into Petri dish and kept at gradually increased temperatures, finally at 230 °C for 1 h.

Magnetic membranes with EC matrix were made by casting of 3 wt% EC solution in 40:60 ethanol/toluene with a dispersed magnetic powder MQP-14-12 (of the appropriate amount: 0.5–1.3 g) in the external field of a coil (stable magnetic field with range of induction 0–40 mT). Magnetic membranes with LPI and HBPI matrices were made by casting of HBPA or LPAA in NMP with a dispersed magnetic powder MQP-14-12 (of the appropriate amount: 0.5–1.7 g) in the external field of a magnet and keeping at gradually increased temperatures, finally at 230 °C for 1 h. For proper dispersion and homogenisation of magnetic particles in the polymer solution, the mixture was sonicated (30 min) using high-intensity ultrasound radiation. After mixing the solutions were poured into the Petri dishes, placed on the levelled plate and evaporated. Membranes were removed from Petri dish (with some distilled water) and dried in 40 °C for at least 2 days before any analysis. With this procedure, a series of membranes with an inorganic content ranging from 47.6 to 87.0 wt% was prepared. Application of the external magnetic field during the membrane casting, inhibited the magnetic particle sedimentation and enhanced the proper particle arrangement. This has enabled us to obtain membranes with perfectly dispersed filler particles

within the polymer matrix. The permeation measurements were performed, before (just powder) and after magnetisation (magnetic membranes). These membranes were magnetised after preparation by a short magnetic impulse using an impulse inductor previously charged to an appropriate voltage, generating magnetic field induction approximately of 2.5 T. Measurements of membrane magnetic induction were carried out using teslameter FH 54. The membranes were stored in a desiccator under the vacuum conditions ($p = 3 \text{ mmHg}$).

2.3. Experimental setup

Experimental setup APG-1, described in paper [35], was used for measurement of the nitrogen, oxygen and synthetic air permeability. Additionally, this setup was furnished with a gas chromatograph HP 5890A, which let us to measure the oxygen and nitrogen concentration in permeate. The main part of this experimental setup is a diffusive chamber, where analysed membrane was put in the form of disc. The membrane effective area was 19.63 cm^2 . This setup was used for a low-pressure (from 0.1 to 1.0 MPa) analysis of gas permeation. Oxygen, nitrogen and synthetic air (21% O_2 and 79% N_2) were supplied to the setup from compressed gas cylinders. After installation of membrane in the diffusive chamber, we have rinsed this chamber with an analysed gas. Then, between high- and low-pressure part of a chamber the suitable pressure difference was established (0.3–0.7 MPa) and controlled by an electronic pressure meter and controller EL-press P-506C (for every analysed membrane). Step change in feed pressure for this controller was shown in figure presented in our earlier paper [35]. It was found that the error of the measurement (about 0.2 s) is very low and is repeatable for all the measurements. It would have a very low and similar effect on all reported diffusion coefficients and hence they could be still compared. After that, the flow rate of permeate was obtained using Flow-Bus flowmeter (with a range 0–3 ml/min) with a computer data acquisition. All measurements were carried out in room temperature. Transport coefficients were calculated, using these flow-rate data and percentage of air enrichment.

2.4. The evaluation of gas transport coefficients

During our research, we have collected experimental permeation data for the oxygen and nitrogen, both for individual, pure gases, as well as components of air and analysed the system, i.e. membrane and permeating gas using appropriate formulas [35], supported by the percentage of the air enrichment. The most fundamental quantity, from many possible is an average diffusion coefficient \bar{D} calculated from the stationary permeation according to the evident formula, i.e.:

$$\bar{D}(\text{cm}^2/\text{s}) = \frac{J_s \cdot l}{\Delta c_0} \quad (1)$$

where J_s is a diffusive mass flux in a stationary state, l is the thickness of membrane and Δc_0 is a concentration difference. We were able to measure the flux (using a flowmeter) and then after integration with respect to time, we have got a downstream absorption permeation, shown in figure $Q^a(l, t)$ (penetrant mass which is flowing out from the membrane ($\text{cm}_3^{\text{STP}}/\text{cm}^2$)) versus time, presented in the paper [35]. Δc_0 was obtained from an intercept of the asymptote to the stationary permeation curve with the $Q^a(l, t)$ axis [35,36,38,39].

Comparing \bar{D} with the value of diffusion coefficient D_L calculated from the downstream absorption time lag [35,36] according to the following equation:

$$D_L(\text{cm}^2/\text{s}) = \frac{l^2}{6L^a(t)} \quad (2)$$

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