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Novel gas separation membrane for energy industry

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ABSTRACT

The aim of the study was to produce membranes with specific separation properties with respect to selected gas mixtures. The attention was focused on mixtures of gases generated in energy industry. To prepare membranes, microporous capillaries made of polypropylene, which served as a supporting layer was used. Next, they were modified by placing a selective layer consisting of block copolymer Pebax and polymer PEO. The obtained results proved the usefulness of developed membrane to gas separation processes in the energy sector.

Keywords: Membranes; Gas separations; PEBAX; PEO

1. Introduction

Studies on the possible use of membrane processes for the separation of gas mixtures have continued to be invariably performed for many years. The development of polymer chemistry enables the production of new types of membranes and provides them with new separation properties. In addition, the economic potential of re-use of industrial wastes as well as increasingly stringent environmental requirements make the world of science explore new methods for purification of gases from undesirable substances. Due to those reasons, a lot of attention is paid to membranes made of polymer material. Currently, polymeric membranes are used on an industrial scale to separate air components (oxygen and nitrogen), to dry air and to remove hydrogen and ammonia from industrial gases. Properties of polymeric materials make it impossible to obtain both, high selectivity and permeability of the membrane, what in general limits the use of such a material in larger scale than laboratory one [1]. Therefore, solutions to overcome this barrier are intensively searched for.

One of the method used to improve membrane separation properties is the introduction of an inorganic components to a membrane polymer matrix, which allow to modify the mechanism of separation, and thus, contribute in solution of Robeson's upper limit problem, usually occurring in polymeric membranes [2,3].

Another solution to this problem is the use of membranes made from copolymers or polymer mixtures, what is the case of the studies discussed in this paper.

Energy industry seeks for solutions dedicated to the separation of various gas mixtures. The most common processes nowadays used in this sector are: drying of natural gas or biogas, separation of nitrogen and carbon dioxide from methane, as well as removal of carbon dioxide from flue gas, which simply means separation of carbon dioxide from nitrogen. Drying of methane streams is widely discussed in other papers written by the authors of this study [4,5]. This paper presents the results of research on other issues, i.e. separation of the following gaseous mixtures: CH_4/CO_2, CH_4/N_2, N_2/CO_2.

2. Materials and methodology for novel membranes production

For the production of composite membranes, microporous polypropylene capillary membranes supplied by Polymemtech were used as the support. The basic parameters of the used support membranes are shown in Table 1.

The selective layer formed on the support was made of two types of polymeric mixtures. In the first case, a mixture

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Table 1
Parameters of Polymemtech polypropylene membranes

Parameter	Value
Outer diameter, mm	2.8
Internal diameter, mm	1.8
Average pore size, µm	0.3
Porosity, %	50–60

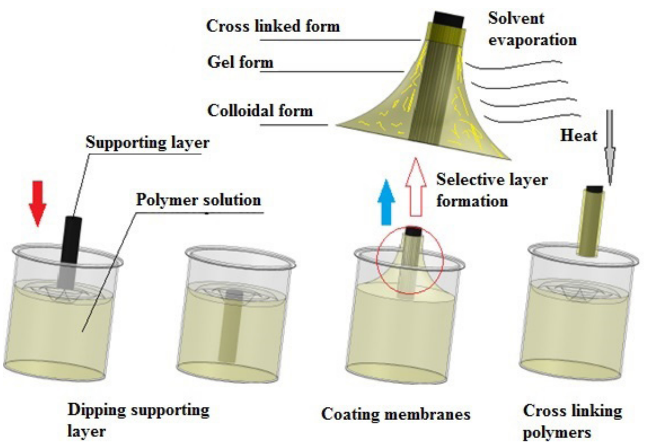

Fig. 1. Process of dip-coating and forming of a selective layer [6].

of copolymer Pebax 1074 and polymer PEO was used, while in the second case a mixture of copolymer Pebax 2533 and polymer PEO was investigated. Both types of copolymer Pebax were supplied by Arkema, while polymer PEO was delivered by Sigma Aldrich. The latter supplier also provided 2-butanol, which was used as a solvent.

The selective layer was produced by dip-coating, as shown in Fig. 1, which was conducted in three stages:

(a) Immersion of a capillary in the polymer solution.
(b) Taking the capillary out with a predetermined speed.
(c) Drying and cross-linking of the membrane at the desired conditions.

The cross linking process may be carried out at atmospheric conditions or in a dryer. With the increase of drying and solvent evaporation duration, the polymer solution changes its form from a colloidal to a gel, and next, depending on the used material, it takes an amorphous or crystalline form. The thickness of such a formed selective layer depends mainly on the concentration of the polymer in the solvent (affecting rheological properties of the solution) and on the speed of ascent of the capillary from the polymer solution. It is possible to obtain a coat of a thickness ranging from several to dozens of micrometers.

The advantage of this method is the repeatability of the process and accurate control of the parameters affecting characteristics of the obtained layer, which are polymer concentration in the solution, the duration of the immersion of the capillary in the solution, the solution temperature, the speed of ascent and the intensity of drying. Main disadvantages of the method are high solvent consumption and possibility of too rapid crystallization of the polymer, which may result in uneven coating, followed by defects in its structure [6].

Different compositions of polymer mixtures used to form the selective layer were studied. Five solutions, which contained 2%, 4%, 6%, 8% and 9% of polymer Pebax 1074 and 8%, 6%, 4%, 2% and 1% of polymer PEO, respectively, in the solvent, were prepared. The same was done for the mixture of polymers Pebax 2533 and PEO. It has been noted that solutions containing 2%, 4% and 6% of polymer were unable to form a properly dense layer on the surface of support membranes. In turn, the solution containing more than 10% of the polymer had a tendency to gel in the contact with the surrounding air. Hence, solutions containing 8% of Pebax and 1% of PEO were chosen for further tests. On the basis of results obtained during test with pure gases, two membranes expected to possess the best properties were chosen. In both cases these were membranes contained 8% of polymer Pebax 1074 or polymer Pebax 2533 and 2% of PEO.

Such prepared composite, capillary membranes were placed in a circular cross section module made of PVC. In the 50 cm long module with a diameter of 25 mm, 10 capillaries were placed in parallel. The total area of the membrane in the module was 0.04 m^2.

2.1. Research equipment

The setup for the gas permeation test consisted of a membrane module and the measuring equipment. Due to the flexible connections, the installation gives the possibility of testing of any membrane module. The setup is equipped with flow meters (high pressure rotameters), temperature and gas pressure (relative pressure) measurement sensors as well as dew point transmitter. The measurements of pressure, temperature, flow rate and humidity (dew point) are performed for the raw gas stream (feed) as well as for permeate and retentate streams. The proper levels of gas flow are achieved by the control valves. Optionally, an independent gas humidifier may be used. The scheme of the installation is presented in Fig. 2.

In order to examine the structure of the membrane, scanning electron microscope Phenom was used. The analysis covered the topography of the side surface and the cross-section of the membrane. For preparation of the sample, the membrane was placed in liquid nitrogen and next broken down. During the analysis, special attention was paid to the

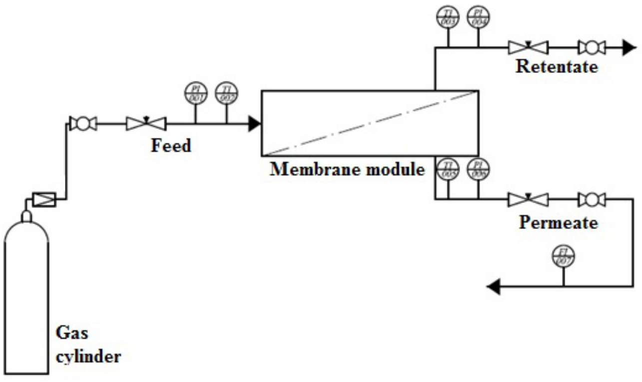

Fig. 2. The scheme of the test installation.

continuity of the selective layer, undesired presence of pores, if any eventually appeared, and the layer thickness.

3. Test results and discussion

Exemplary microscopic images of the produced membranes are presented in Fig. 3. The analysis of these images indicated that the resulting selective layer characterized by an acceptable uniformity, no discontinuity of the structure was found.

For calculation of permeate flux Fick's equation, Eq. (1), was used. One can note a relationship between the permeate flux and the driving force, the pressure in this case [7], is linear.

$$J = P\frac{\Delta p}{l} \tag{1}$$

where, J is the permeate molar flux [mol·s^{-1}·m^{-2}], P is the permeability [barrer], Δp is the pressure difference [Pa], l is the membrane thickness [m]. The permeability coefficient is given in barrer. It is not a SI unit, but it is a generally accepted unit for membrane gas separation processes, which can be defined as in Eq. (2):

$$1\ \text{barrer} = 3{,}35 \cdot 10^{-16}\,\frac{\text{mol}\cdot\text{m}}{\text{Pa}\cdot\text{s}\cdot\text{m}^2} \tag{2}$$

The measurements of the volumetric flow rate of permeating gases were obtained during tests with pure components (CH_4, CO_2, N_2) at increasing pressure. The measurement results are shown in Table 2. Because of almost unmeasurable low flows of permeate at lower feed pressure, some of the results are given only for higher pressures. Table 2 presents the average results of 10 measurements related to normal conditions. In Figs. 4–6, graphs of the pure gaseous components flow through the membrane in dependence of the feed pressure, are shown. The analysis of these graphs indicated that the theoretical linear relationship, (see Eq. (1)), was preserved between the volumetric flow rate under normal conditions and the feed pressure. This observation was also relevant for the CO_2. The linear relationship allows to conclude that the membranes do not undergo plasticization eventually caused by an interaction with carbon dioxide.

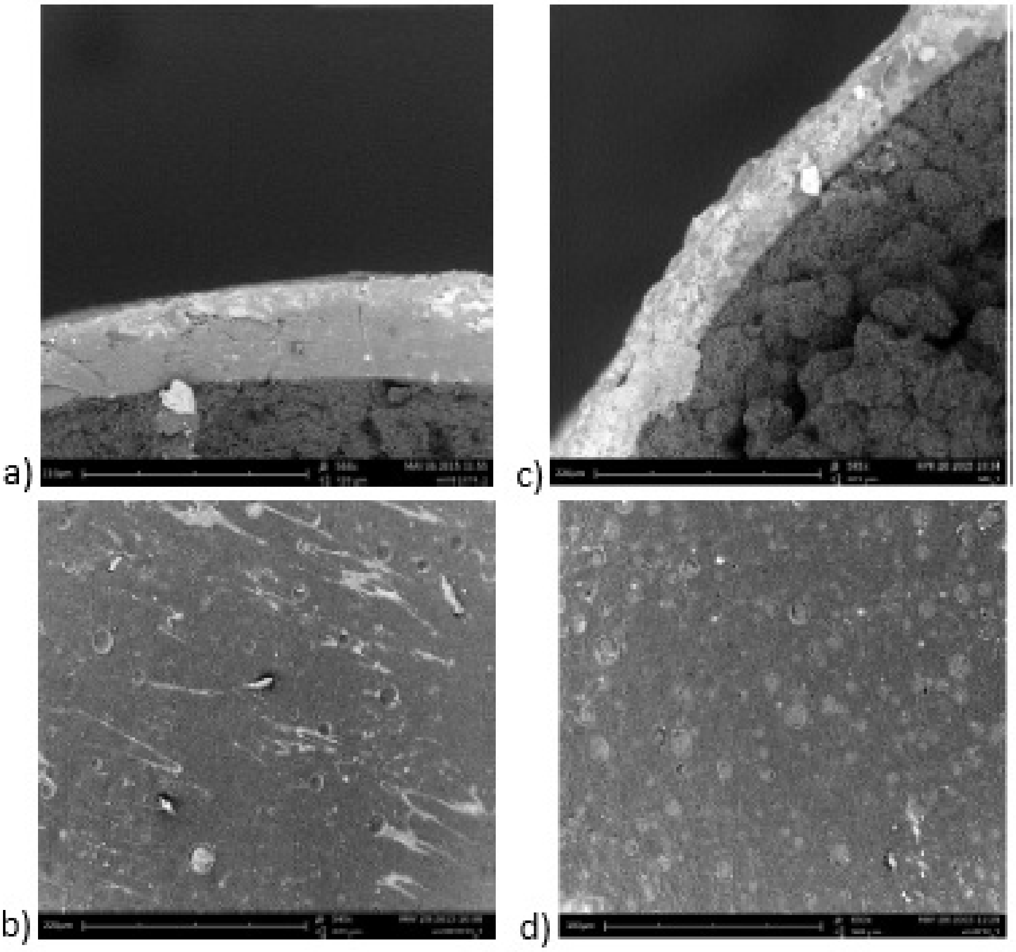

Fig. 3. Cross section and external surface of membranes made from polymers PEBAX 2533 and PEO (a) and (b), and PEBAX 1074 and PEO (c) and (d).

Table 2
Volumetric flow rate of the permeate obtained duringpure component measures at different feed pressures

Membrane composition		Volumetric flow rate of permeate [cm³ min⁻¹]	Feed pressure [bar]		
			1	2	3
PEBAX 1074 8%	PEO 2%	Q_{CH_4}	–	–	0.2
		Q_{CO_2}	1.9	3.3	4.7
		Q_{N_2}	–	–	0.15
PEBAX 2533 8%	PEO 2%	Q_{CH_4}	1.3	2.6	4
		Q_{CO_2}	6.7	12.8	19.2
		Q_{N_2}	0.5	1.1	1.7

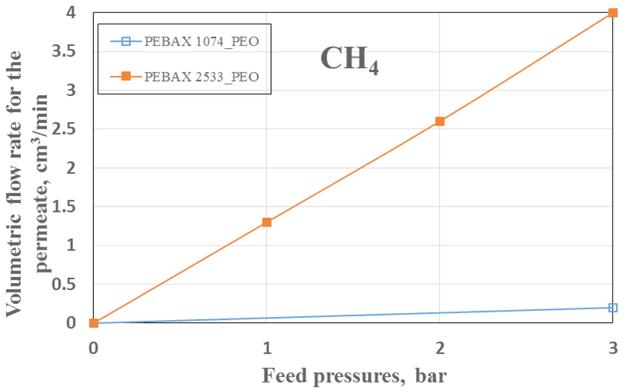

Fig. 4. The dependence of the volumetric flow rate of pure methane on the feed pressure.

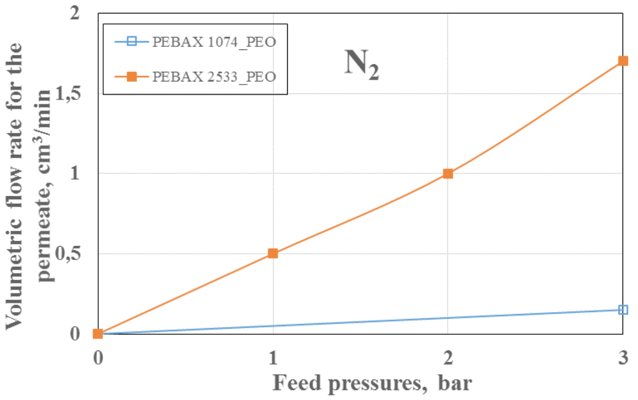

Fig. 5. Dependence of the volumetric flow rate of pure carbon dioxide on the feed pressure.

Using both, the data collected in Table 2 and Eq. (1), membrane permeabilities were determined and collected in Table 3. Since an ideal selectivity factor, α, is a quotient of pure gases permeabilities, respective separation factors are collected in Table 4.

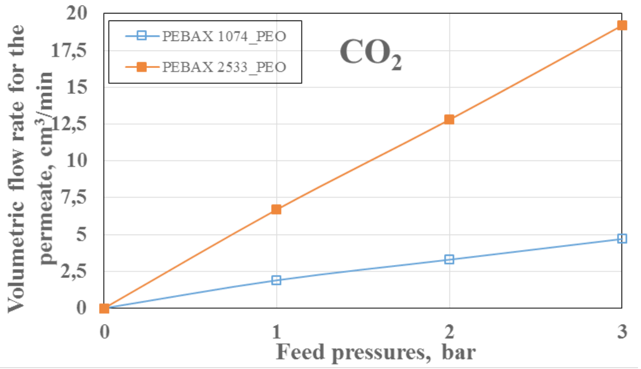

Fig. 6. The dependence of the volumetric flow rate of pure nitrogen on the feed pressure.

Table 3
Permeation coefficient obtained during pure components measures at different feed pressures

Membrane composition		Permeation coefficient [barrer]	Feed pressure [bar]		
			1	2	3
PEBAX 1074 8%	PEO 2%	P_{CH_4}	–	–	1.8
		P_{CO_2}	35	34.1	35.7
		P_{N_2}	–	–	1.4
PEBAX 2533 8%	PEO 2%	P_{CH_4}	28	27.2	28.6
		P_{CO_2}	142.9	136.2	136.9
		P_{N_2}	10.5	11.6	11.9

Table 4
Membranes selectivity obtained during pure component measures

Membrane composition		Selectivity [–]	
PEBAX 1074 8%	PEO 2%	α_{CO_2/CH_4}	19.4
		α_{CO_2/N_2}	24.9
		α_{CH_4/N_2}	1.3
PEBAX 2533 8%	PEO 2%	α_{CO_2/CH_4}	5
		α_{CO_2/N_2}	11.6
		α_{CH_4/N_2}	2.3

By adopting generally accepted assumption, that the membrane permeability for a pure component is independent of the feed pressure, average permeability results obtained for different pressures were calculated. The average membrane permeability for pure components allowed to determine the selectivity of the membrane for two gas components mixture as the quotient of membrane permeability of these particular components.

In the literature, one can find Robeson's paper, in which separation properties of hundreds of polymers are collected in one chart [8]. The comparative analysis of the results obtained for the developed membranes with ones discussed in [8] indicated that, in terms of performance characteristics (permeability, selectivity), the results of the developed membranes were similar to the results obtained for other polymers. A significant difference between the results in [8] and the current results were found for membrane surface and thickness. The vast majority of the published results on permeability and selectivity of polymers is given for membranes of a very small surface and relatively large thickness at the same time. This study presents the research results obtained for modules, which that due to the repeatable method of membranes preparation, can have any size of the surface, while their thickness is acceptable for any industrial use.

4. Conclusions

(1) New membrane modules comprised of composite membranes of the thickness acceptable for any industrial use were developed. The membrane surface in the module can be, easily increased if needed.
(2) Performance characteristics of the developed membranes are comparable to theoretical possibilities offered by recent state of the art.
(3) The linear relationship between the flow rate of the permeate and the pressure observed during the study confirms the theoretical assumptions. In case of carbon dioxide permeation, it also indicates that no plasticization of the membrane material, its after interaction with the gas takes place.
(4) Obtained values of permeability and selectivity given for the selected pairs of gases indicate that these membranes can potentially be used in energy industry for separation of particular components of gaseous mixtures such as CH_4/CO_2, CH_4/N_2, N_2/CO_2.

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