GAS SEPARATION MEMBRANES MADE OF PEBA BLOCK COPOLYMER

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Abstract

Membranes made of PEBA block copolymer have very interesting separation properties for gas pairs where CO_2 appears. Using these membranes, one can remove CO_2 from the various gas streams. Owing to this property, the use of these membranes for processing of natural gas or gas streams obtained from biomass conversions appears to be of great interest. Flat membranes and composite capillary membranes both made of copolymer PEBA have been prepared and their separation properties have been investigated. Primary tests have been conducted for CO_2 and N_2 using commercial polymer Pebax® 1074.

Streszczenie

Membrany wykonane z kopolimeru blokowego PEBA posiadają interesujące właściwości w rozdzielaniu mieszanin gazowych, w których jednym ze składników jest CO_2. Dzięki membranom wykonanym z tego polimeru możliwe jest usuwanie CO_2 z różnych strumieni gazowych. Dzięki takim właściwościom membrany wykonane z kopolimeru PEBA cieszą się dużym zainteresowaniem w procesach uzdatniania gazu ziemnego oraz w procesach oczyszczania gazu powstałego z biomasy. Praca prezentuje wyniki prób wykonania membran płaskich oraz kompozytowych membran kapilarnych z kopolimeru PEBA. Przedstawiono wyniki badań separacji mieszaniny N_2 i CO_2 na membranach wykonanych z komercyjnie dostępnego kopolimeru o nazwie Pebax® 1074.

K e y w o r d s : **Membranes; Gas separation; Peba.**

1. INTRODUCTION

In recent years there has been a growing interest towards membrane gas separation techniques. This is driven by the necessity to implement novel energy efficient processes that focus on the environmental protection. Further important point is the optimization of production costs.

Processes employing conventional glassy membranes are not able to yield gas purities at the levels that can be guaranteed by competing processes, e.g. absorption, adsorption, cryo-technique. However, in some cases when very high purity is not required, these methods can be replaced with membrane processes, which makes it possible to implement innovation into the production technology and lower production costs.

Applying membranes for gas separation, one can reduce waste streams such as exhausted sorption materials. It is also possible to save energy in comparison to thermal processes (cryo-technique) or sorption bed regeneration.

The advantage of membrane techniques is also their simple construction and exploitation in comparison to other gas processing methods. It is assessed that membrane plants for gas separation are 5-times smaller than conventional (sorption or thermal) plants.

PEBA copolymer has drawn our attention because of its interesting separation properties. In particular, a very interesting property is its reverse selectivity for CO_2 and H_2. It means that the bigger particle, CO_2, goes faster through the membrane than the smaller one, H_2. This phenomenon can be explained by interaction between the CO_2 molecule (having quadruple moment) and polyether segment in copolymer [1]. Owing to this property, the removal of CO_2 from the streams with hydrogen or methane may be economically viable.

Moreover, H_2S (dipole moment) permeates faster through PEBA membrane than hydrogen or methane; it was proven by us in other experiments. Thus PEBA membranes can be applied in such processes as desulphurization of biogases.

2. MATERIALS AND METHOD

We have prepared for our experiments polymeric membranes made of block copolymer PEBA, trade name Pebax®. General formula of this substance can be shown as follows:

where PA is the polyamide segment and PE is the polyether segment.

$$HO \left[\overset{O}{\overset{\|}{C}} - PA - \overset{O}{\overset{\|}{C}} - O - PE - O \right]_n H$$
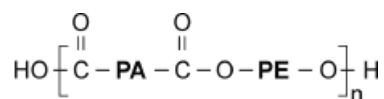
Pebax® denotes a group of block-co-polymers that can be characterized by different mass ratio of PA and PE segments. We have decided to implement Pebax® 1074, where mass ratio of PE/PA is 55:45 [2].

In the literature a variety of methods for the preparation of PEBA membranes can be found. For example, as far as the concentration of the polymer in the solvent is concerned, 2% of the polymer in solution [2] or 6% and 15% [3] were chosen. As a solvent n-butanol [2] or 1-methyl-2-pyrolidone (NMP), 1-butanol, isopropanol and dimethylacetyamide (DMAc) [3] were used.

In our experiments, we have prepared 5% of Pebax in 2-butanol solution. Pebax® 1074 was delivered by Arkema and pure 2-butanol by Merck.

The solution prepared in adequate proportion (poly-

mer in granulated form) were placed in a glass flask with a cooler. The solution was heated to the boiling temperature and intensively stirred for 4 days. After that the homogenous solution was degassed.

Using this solution, flat membranes and composite capillary membranes were prepared.

Flat membranes were spilled on a warm glass plate and leveled by a special casting knife. After that membranes were kept in controlled temperature for the purpose of solvent evaporating. The next step was taking off the membrane from the glass plate. Ready membranes were conditioned for a few days in controlled temperature and humidity. The air inside the conditioning chamber was continuously changed in order to remove solvent vapour.

The obtained membranes had thickness in the range of a few to a few dozen microns depending on the casting knife settings. All thickness measures were made using SEM images.

Membranes prepared of Pebax® 1074 as flat sheets are colorless and transparent. They are elastic and durable.

Composite capillary membranes were prepared on the polypropylene support. As a support Polymem Ltd microfiltration membranes were used. The external diameter of capillaries was 2.6 mm.

We have decided to coat polypropylene membranes by Pebax using a well known method of dip-coating. We have plunged capillaries 6 times into the warm solution of PEBA copolymer. Between each plunge membranes were kept in controlled atmosphere for
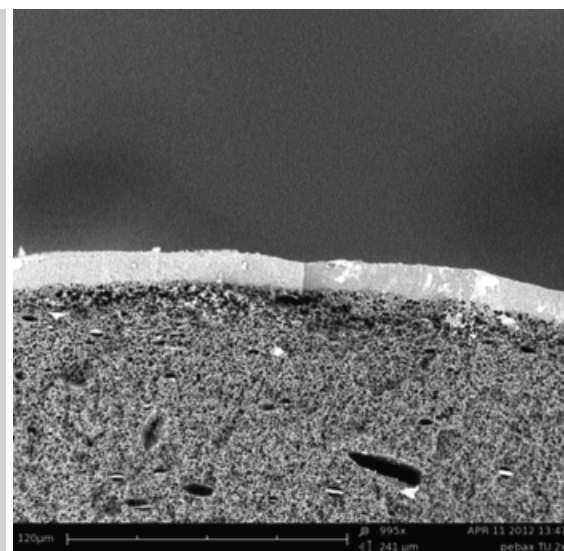
Figure 1.
Cross section of the composite capillary membrane. Selective layer prepared of Pebax® 1074. Magnification 995x

about 1 hour. In Fig. 1. cross section of the composite capillary membrane is shown. Average thickness of its selective layer is ca. 15 microns.

Analyzing SEM pictures of our membranes we can state that the obtained membranes have non-porous morphology.

3. SEPARATION EXPERIMENTS

In our experiments, we have examined only flat membranes but we expect separation properties of capillary composite membranes to be the same.

For the examination of separation properties an automated setup was used. This setup was constructed by Institute of Chemical and Process Engineering, Vienna University of Technology. It allowed us to conduct the separation process under controlled conditions (pressure and flow). The membrane module was situated in a chamber with stable temperature. Gas flows were measured with flowmeter Definer 220H by Bios.

For experiments we have used flat membrane of 3.7 μm thickness and 80 cm^2 area. This flat Pebax membrane was supported by polypropylene microfiltration flat membrane. Experiments were conducted in the dead-end configuration. The permeate chamber was open to the atmosphere.

Fig. 2. to Fig. 6. present results that were obtained during pure gases permeability measurements. Pressure and feed temperature were changed for individual measurements.

Permeance, P, was obtained on the basis of the following formula:

$$P = \frac{N}{\Delta p} \qquad (1)$$

where N is molar flux – in this case it is volume of gas in standard temperature and pressure, Δp is the difference of pressure at feed side and permeate side. Permeance was presented in unit GPU (gas permeation units); in SI it is equal to 10^{-6} cm$^3_{STP}$/(cm^2·s·cmHg). A permeance of 1 GPU is when 1 μm thickness membrane has permeability of 1 barrer.
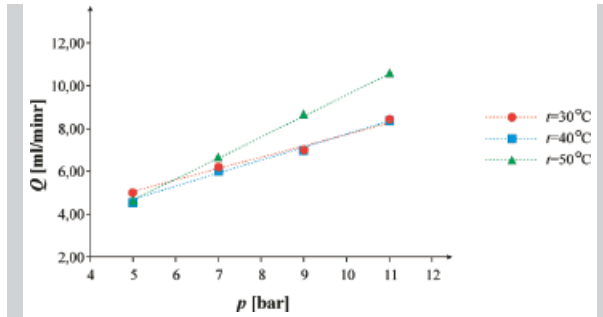

Figure 2.
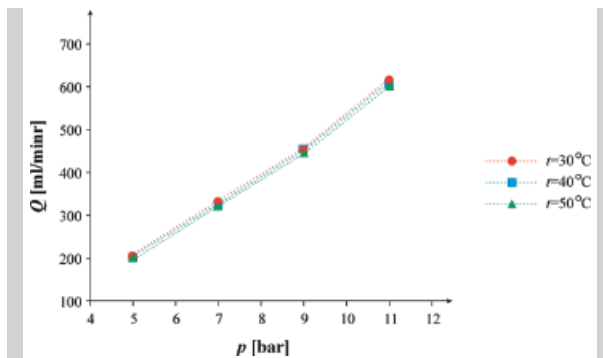**Permeate flow versus pressure for nitrogen**

Figure 3.
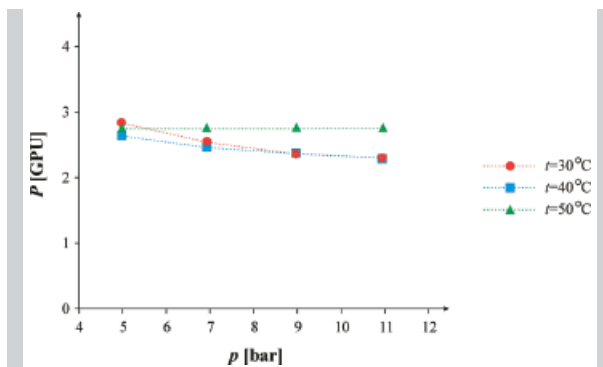**Permeate flow versus pressure for carbon dioxide**

Figure 4.
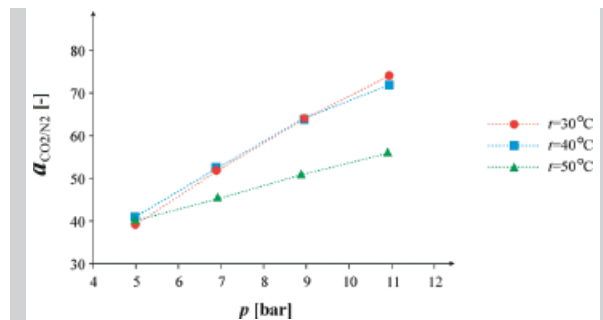**Permeability for nitrogen versus pressure**

Figure 5.
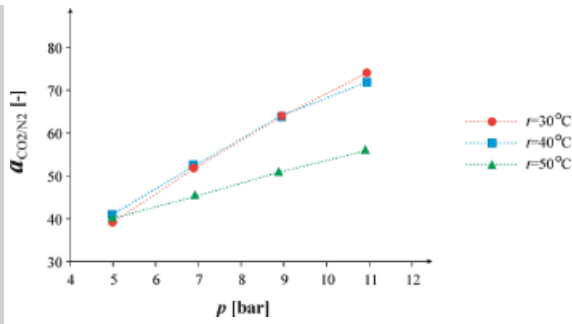**Permeability for carbon dioxide versus pressure**

Figure 6.
Ideal selectivity CO$_2$/N$_2$

4. DISCUSSION

Each point in curves in Fig. 2. – Fig. 6. is the result of averaging 3 measurements. It is important to note that repeatability of results was very high. It shows that the process was stable. In the first stage of the experiment, we have investigated nitrogen as the first, and carbon dioxide as the second.

Based on literature data [2, 3, 4], we have expected the nitrogen flow to be smaller than the carbon dioxide flow.

It is worth noticing that for nitrogen a linear relationship between the flow and the transmembrane pressure was obtained (Fig. 2). Such a relationship was expected on the basis of the formula Eq.(1). As one can see in Fig. 4., changes of permeability for nitrogen were very small.

In case of carbon dioxide permeation a nonlinear relationship between the flow and the pressure was obtained (Fig. 3). It is roughly an exponential function. It is a consequence of variability of permeability with pressure for carbon dioxide (Fig. 5). As one can see in Fig. 5., this relationship is monotonically increasing and simultanously it is insensitive to temperature changes. Now we are not able to state what the reason of such variability is. It could be caused by polymer plastification or membrane and support interaction.

The results of permeability, shown in Fig. 4. and Fig. 5, are comparable with the results presented for PEBAX/PEI composite membranes in other experiments [4]. In the work [4] another PEBA copolymer was used – Pebax® 2533. Some differences in the results presented in our work and the work [4] can
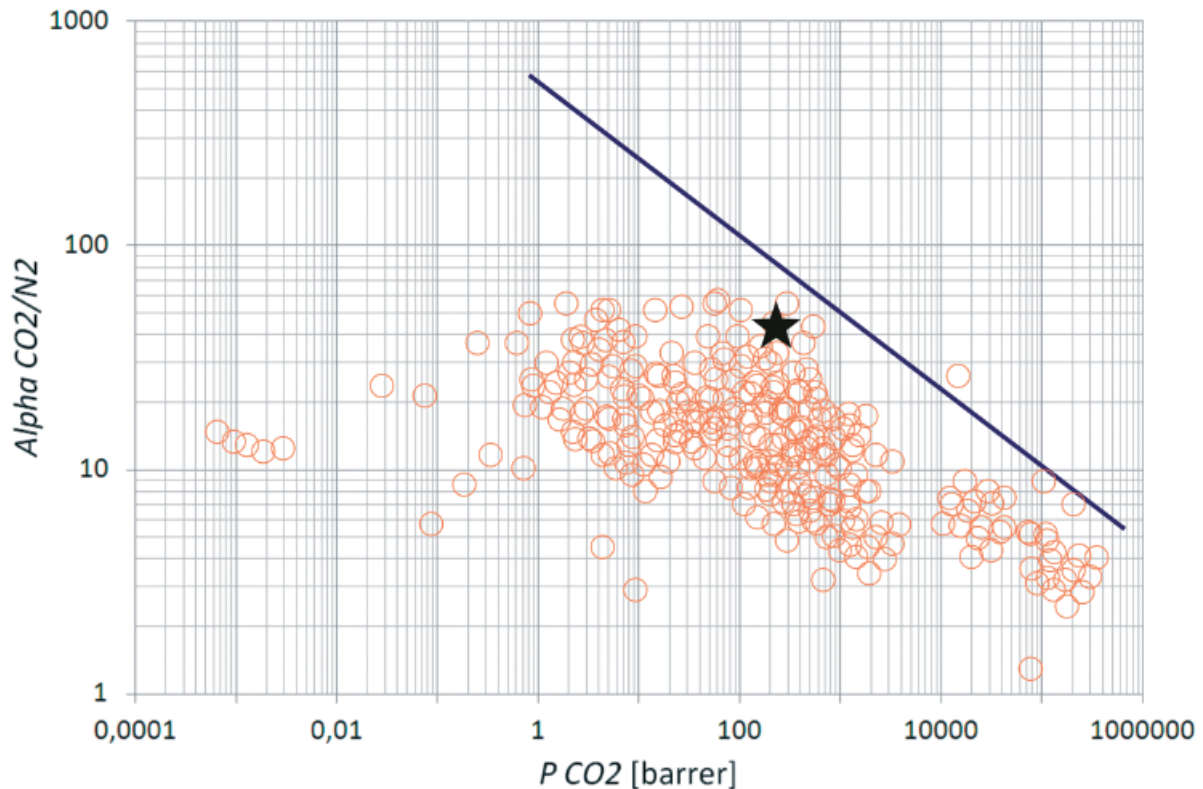

Figure 7.
Selectivity of CO$_2$/N$_2$ as a function of CO$_2$ permeability. Black star represents results obtained in this work (diagram on the basis of [5])

stem from some reasons: differences in copolymer molecular structure (also other PA and PE proportions) and support membrane structure. Our membrane was not a really composite membrane only a supported one.

Separation ability of the membrane made of Pebax® 1074 was characterized by using ideal selectivity. We have used for this purpose a generally accepted formula describing an ideal selectivity [1]:

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \qquad (2)$$

In equation (2), adequate for every pairs of gases, in numerator there is permeability of the faster gas. Thus the ideal separation factor is greater than 1.

Separation ability of membrane calculated using Eq. (2) is presented in Fig. 6. Because permeability for nitrogen as a function of pressure is constant and permeability for carbon dioxide is increasing, ideal separation factor for CO_2 and N_2 is also an increasing function of pressure. The value of this factor in examined pressures is in the range 40-70.

Reasuming the results presented in Fig. 2 – Fig. 6., one can state that nitrogen and carbon dioxide separation by membranes is possible and more effective (greater flows and greater separation factor) for higher pressures. However, this thesis should be confirmed by tests conducted for a real mixture of these two gases.

One can compare our results with other results obtained for different polymers. This comparison could be done using a well known diagram proposed by Robeson [5]. The diagram for nitrogen and carbon dioxide taken from Robeson's work [5] with marked results of our experiments is presented in Fig. 7.

One can see that the membrane made of Pebax® 1074 has very good parameters in comparison to other polymeric membranes. Point (star) describing the Pebax membrane in diagram in Fig.7 lies near the upper boundary line – which means it lies near the hitherto determined empirical limit for polymeric membranes in gas separation processes. The value of permeability of CO_2 has been obtained by calculation of permeance and membrane thickness.

5. CONCLUSIONS

Lab-scale technology of polymeric membranes made of Pebax® 1074 was successfully developed. The prepared membranes have programmable thickness in the range of a few to a few dozen microns. Using different polymer concentration and different conditioning parameters (temperature and air changing velocity) we were able to achieve different thickness of membranes.

Primary experiments conducted with pure gases show that the Pebax membrane is adequate for separation of nitrogen and carbon dioxide.

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