

Final Draft
of the original manuscript:

Car, A.; Yave, W.; Stropnik, C.; Peinemann, K.-V.:
**Pebax/polyethylene glycol blend thin film composite membranes
for CO₂ separation: Performance with mixed gases**
In: Separation and Purification Technology (2008) Elsevier

DOI: 10.1016/j.seppur.2008.01.001

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

Anja Car^{a,b,*}, Wilfredo Yave^b, Chrtomir Stropnik^a, Klaus-Viktor Peinemann^{b,*}

^a **University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia**

^b **GKSS-Research Centre GmbH, Institute of Polymer Research, Max-Planck-Str. 1, 21502 Geesthacht, Germany**

Abstract

The paper describes the performance of Pebax[®]/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 293K up to 20 bar. Improved permeabilities and CO₂/H₂ selectivities were obtained in the newly developed composite membranes

Keywords: Pebax, thin film composite membranes, CO₂ separation, mixed gases.

1. Introduction

Today's industrial production and infrastructure in the world is 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.

Table 1: Typical CO₂ concentration in process streams [3]

Process	CO₂ conc. [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

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]. To its removal, a wide variety of technologies are available. They include absorption, cryogenic and iron sponge 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 70ies, 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 Table2).

Table 2: Gas membrane application and suppliers [9]

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 Praxar
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) Kvarner, Air Products Ube
H ₂ S/hydrocarbon	Sour gas treating	as above
H ₂ O/hydrocarbon	Natural gas dehydration	Kvarner, Air Products
H ₂ O/air	Air dehydration	Air Products, Parker Balston Ultratroc, Praxair
Hydrocarbons/air	Pollution control hydrocarbon recovery	Borsing, MTR, GMT NKK
Hydrocarbons from process stream	Organic solvent recovery Monomer recovery	MTR, SIHI, GMT

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 permeant 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 environmentally friendly solvents during the membrane preparation.

It was shown that polyamide-polyether (Pebax[®]) block copolymers could fulfil above mentioned requirements especially due to its 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 2h (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 1h. 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 penetration of PEG 200 into the microporous structure of PAN support. The coated support was then dipped into the solution containing Pebax and PEG. After the dip coating procedure, the membranes were dried in air at room temperature.

2.2 Gas permeation experiments

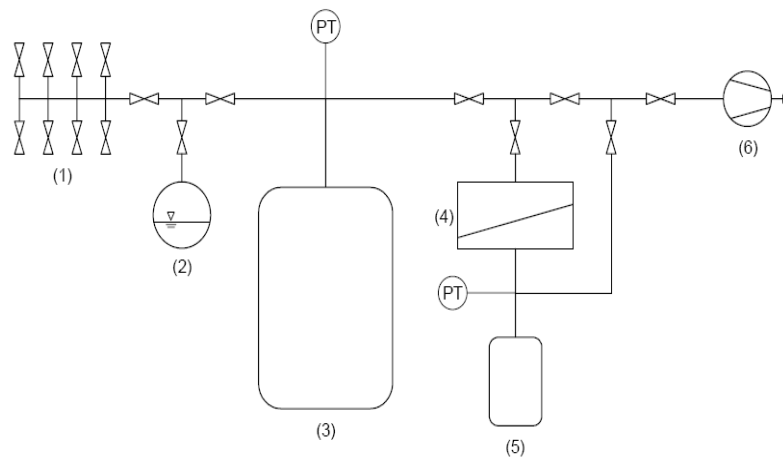
A pressure increase test unit designed and built by GKSS (Scheme 1) was used to measure the permeability of single gases (H₂, N₂, CH₄ and CO₂) at different temperatures (from 283 to 333 K) and 1 bar of feed pressure. The permeance values of a membrane with an unknown thickness of the selective layer are called flux (J), which can be calculated using equation 1:

$$J = \frac{V \cdot 22,4}{R \cdot T \cdot A \cdot t} \cdot \ln \left(\frac{p_F - p_0}{p_F - p_{p(t)}} \right) \quad (1)$$

where V is the permeate volume, R the ideal gas constant, T the temperature, A the membrane area, t is time of measurement, and p_F , p_0 and $p_{p(t)}$ are the pressures at the feed, permeate side at beginning and at the end of measurement, respectively. The single gas selectivity (α) between two components A and B can be expressed by equation 2:

$$\alpha_{AB} = \frac{J_A}{J_B} \quad (2)$$

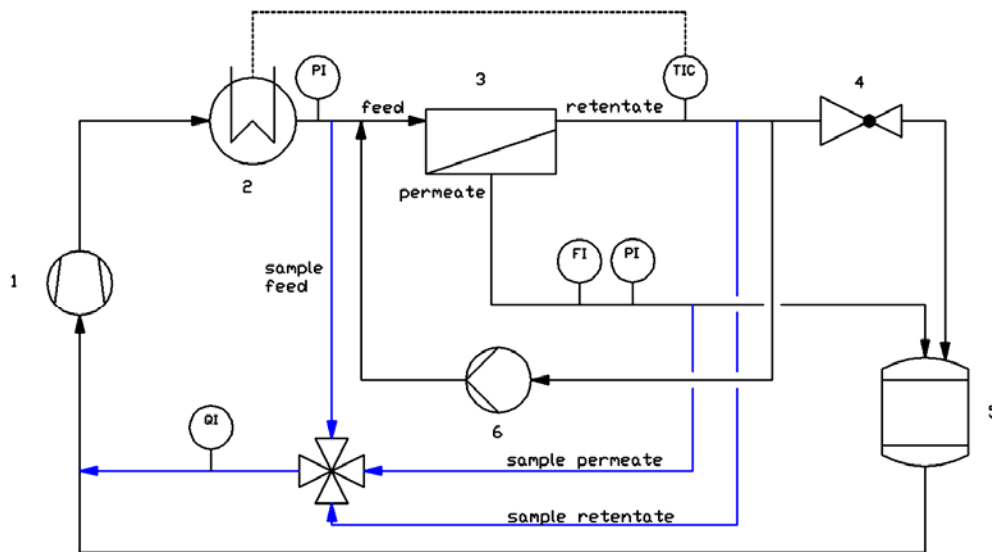
The test unit which is shown in Scheme 1 is suitable to perform permeance (flux) tests with various gases and vapours.



Scheme 1: Pressure increase test unit: (1) gas inlet, (2) chamber for liquid samples, (3) feed pressure volume, (4) membrane test cell, (5) permeate volume, (6) vacuum pump, and (PT) pressure sensor.

The flow rate of single gases at different pressures (up to 20 bars) and 293K was tested with a similar device described above, with the difference that fluxes were measured manually by using a bubble meter (Bioblock Scientific).

Mixed gas measurements of CO_2/H_2 , CO_2/N_2 and CO_2/CH_4 were carried out at feed pressure up to 20 bar and 293 K, by using a device as shown in Scheme 2. Permeate pressure was approximately 1.1 bar and the stage-cut (ratio permeate flow to feed flow) during the measurements was less than 1%. The feed compositions for CO_2/H_2 and CO_2/CH_4 were 50/50 vol. %, and for CO_2/N_2 mixture was 25/75 vol. % respectively.



Scheme 2: High pressure device for mixed gas measurements: 1) compressor, 2) heat exchanger, 3) membrane test cell, 4) pressure reduction valve, 5) vessel, 6) gas circulator,

(PI) pressure indicator, (TIC) temperature indicator and controller, (FI) flow rate indicator and (QI) quality indicator (gas chromatograph).

The facility allows studying permeation of mixed gases through the flat composite membranes [21]. The compositions of the feed, retentate and permeate side were analyzed by a gas chromatograph (Variant 3400 with column Chromosorb 107), and the flux of gases was determined by the following equation (3):

$$J_A = \frac{V_{P,A}}{A_m \cdot (f_{R,A} - f_{P,A})} \quad (3)$$

where V_P represents permeate volume flow rate, A_m is the membrane area, f_R and f_P are fugacities of retentate and permeate. The fugacity [22] for a gas (A) was calculated using equation (4):

$$f_A = \Phi_A \cdot x_A \cdot P \quad (4)$$

where the fugacity coefficient Φ_A was determined by Redlich-Kwong-Soave [23] equation, using Aspen Plus, x_A represents the molar fraction of gas A, and P is the total pressure.

The selectivity of membrane for mixed gas was also calculated by equation (2); the area of all membrane samples was 35 cm².

All data presented in this work were collected as follows: at least three samples were tested for single and mixed gas at different pressure; for temperature dependence, one sample per series of gases was used.

2.3 Morphology characterization

The thickness and surface morphology of composite membranes were analyzed by scanning electron microscopy (SEM). The SEM analyses was carried out with a LEO 1550 VP Gemini (ZEISS) microscope.

3. Results and discussion

3.1 Single gas measurements

Temperature dependence

Temperature effects on membrane performance were studied in the temperature range of 283-333 K (single gas at 1 bar feed pressure).

The CO₂ flux for different Pebax[®]/PEG membranes versus the reciprocal temperature is presented in Figure 1. Higher temperatures enhance the gas flux due to the increased motion of polymer chains, and thus the diffusivity of CO₂ is increased [24]. In pure Pebax[®] and all Pebax[®]/PEG blend composite membranes, the CO₂ flux increased by nearly 90% when the operating temperature was changed from 303 K to 333 K. This behaviour is a typical Arrhenius type of relation (will be discussed below), which is typical for nonporous polymeric membranes (the higher the temperature, the higher the gas flux) [25]. As can be seen in Figure 1, the Pebax[®]/PEG blend membranes exhibit higher CO₂ flux compared to membranes prepared from pure polymer, similar results were reported previously for homogeneous films [20]. High CO₂ flux in Pebax[®]/PEG blend membranes is attributed to the presence of additional EO units by the addition of PEG which increases CO₂ solubility, and probably induce an increase in of fractional

free-volume. Although the flux is enhanced with temperature increase, the selectivity of CO/H₂, CO₂/N₂ and CO₂/CH₄ is declined (see Figure 2). Therefore, it implies that CO₂ flux and selectivity must be compromised (optimized) between productivity and high purity of gases according to the application.

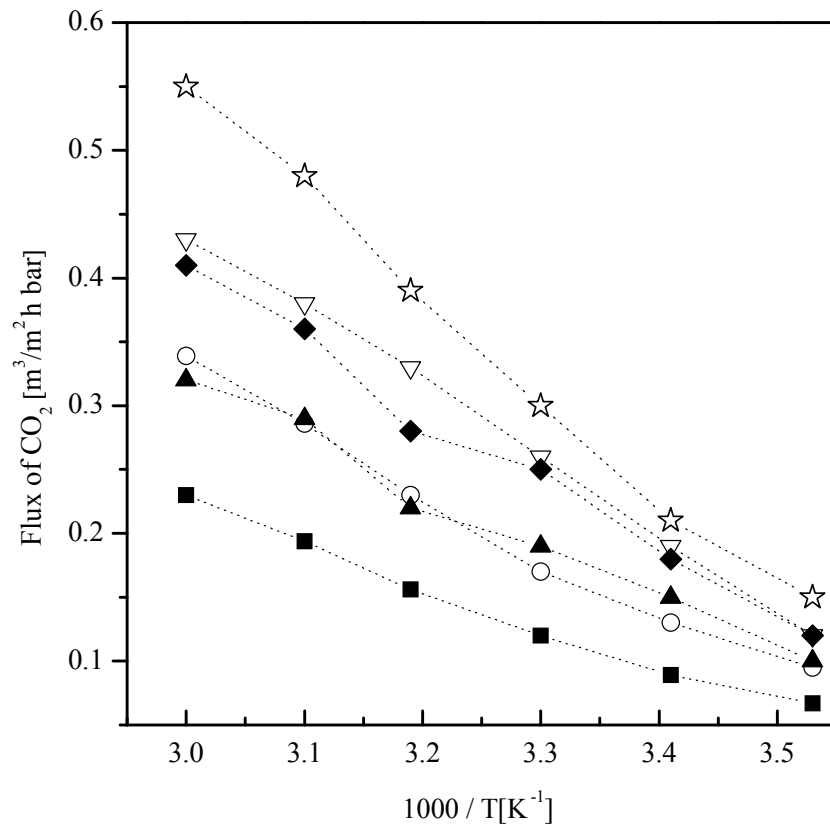


Figure 1: CO₂ flux for Pebax[®] and Pebax[®]/PEG membranes as a function of reciprocal temperature. (-■- 0% PEG, -○- 10% PEG, -▲- 20% PEG, -▽- 30% PEG, -◆- 40% PEG and -☆- 50% PEG).

At all operating temperatures, Pebax[®]/PEG blend membrane with 50 wt. % PEG content presented higher CO₂ flux (more than 2 fold) compared to the pristine Pebax[®]

membrane. The high carbon dioxide flux obtained is quite attractive for technical application of this blend membrane. As next step testing under real conditions is necessary.

Whereas gas fluxes increased with PEG content, blend composite membranes kept almost the same selectivity for most temperatures compared to pristine Pebax[®] (Figure 2). A significant difference at lower temperature was observed. Selectivity for CO₂/N₂ at 333 K is nearly 30; at 283 K it reaches 80 approximately, CO₂/CH₄ selectivity is around 25 at low temperature (283 K) and 10 at elevated temperature (333 K). The most interesting results were observed for CO₂/H₂ selectivity, where the best selectivity (approximately 12) was obtained in blend membrane with 50 wt. % of PEG content at 283 K. The CO₂ flux at this operating temperature was 0.15 m³/m² h bar, which is higher than for pristine Pebax[®] at 303 K. Therefore, as reported in our previous paper [20] Pebax[®]/PEG blend membranes outperform pure Pebax membranes.

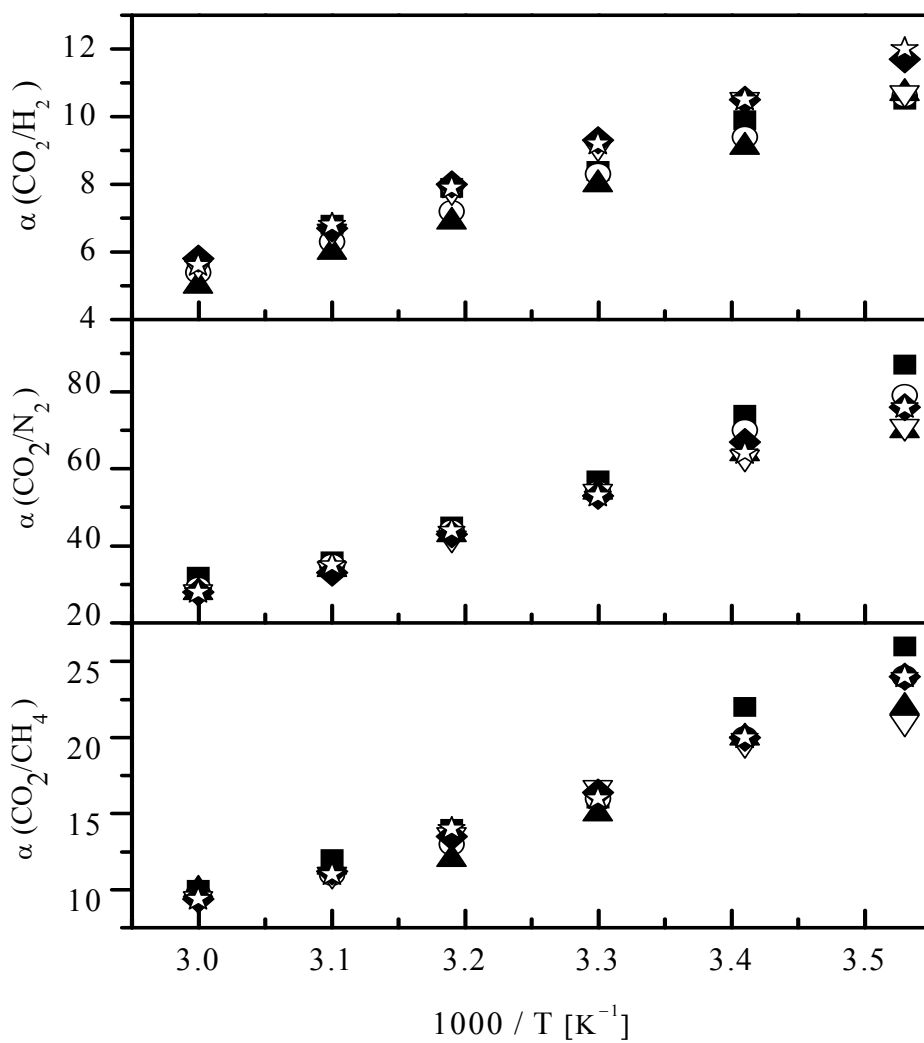


Figure 2: CO₂/H₂, CO₂/N₂ and CO₂/CH₄ selectivity as a function of reciprocal temperature. (-■- 0% PEG, -○- 10% PEG, -▲- 20% PEG, -▽- 30% PEG, -◆- 40% PEG and -☆- 50% PEG).

In order to explore the temperature dependence of CO₂, H₂, N₂ and CH₄ fluxes in these membranes, resulting data were correlated with the Arrhenius equation. This

equation is used to correlate permeability/flux and temperature [25]. Thus, the activation energy of permeation (E_p) can be determined by using the Arrhenius expression (equation 4):

$$J = J_0 \exp\left(\frac{-E_p}{RT}\right) \quad (4)$$

where J is gas flux, J_0 is a pre-exponential factor (independent of temperature) with the same unit as the flux, R the gas constant and T the absolute temperature. The given equation is valid in a temperature range which does not cause significant thermal transitions in the polymer.

Table 3 presents the activation energy of permeation for all gases tested in this work. The PEG addition into the Pebax[®] matrix leads to lower values of activation energies for all gases. As it is known, the sum of activation energy of diffusion (E_D) and the heat of sorption (H_S) is the apparent activation energy of permeation (E_P) [26]. Therefore, in Pebax[®]/PEG samples, the E_P can be affected from both E_D and H_S due to the plasticizer (low molecular PEG) and EO unit present in the system, respectively, and thus, the CO₂ permeation will be affected strongly. The plasticizer increases the polymer chain mobility (gas diffusion increase) and the EO units enhance the sorption of CO₂ in the polymeric system [27].

Table 3: Activation energies of permeation for CO₂, H₂, N₂ and CH₄

Sample	PEG content [wt.%]	E _p [kJ/mol]			
		CO ₂	H ₂	N ₂	CH ₄
Pebax [®]	0	22.2	33.5	40.1	37.6
Pebax [®] /PEG10	10	19.9	31.5	37.3	35.4
Pebax [®] /PEG20	20	18.6	30.2	34.4	33.3
Pebax [®] /PEG30	30	18.5	30.3	34.6	32.8
Pebax [®] /PEG40	40	18.8	30.1	34.1	33.4
Pebax [®] /PEG50	50	17.6	29.8	34.1	32.5

The highest decrease of E_p (26 %) can be noticed for CO₂ permeation in blends with 50 wt. % of PEG; apparently the PEG presence simultaneously affects E_D and H_S . This behaviour is attributed to the polymer polarity changes due to the addition of EO units into the matrix, which mainly influences the CO₂ transport [20, 28]. The E_p for other gases (H₂, N₂ and CH₄) decreased approximately by 12-16%, which can be attributed to the increased motion of polymer chains as result of its temperature dependence, since these gases (H₂, N₂ and CH₄) do not show strong interaction with EO units.

Pressure dependence

Before testing the membranes in a gas mixture, single gas (CO₂, H₂, N₂ and CH₄) measurements were carried out at high pressure. As described in the experimental part, the tests were performed at 293K up to 20 bar. These conditions were selected in order to compare them with gas mixture measurements.. Figure 3 show the CO₂ flux as a function

of fugacity. For all samples (Pebax[®] and Pebax[®]/PEG blend membranes) the CO₂ flux increased when the feed pressure (fugacity) increased from 5 to 20 bar. In rubbery polymers, the solubility coefficient is determining and it strongly depends on gas condensability, especially when strong permeant-polymer interaction exist [29].

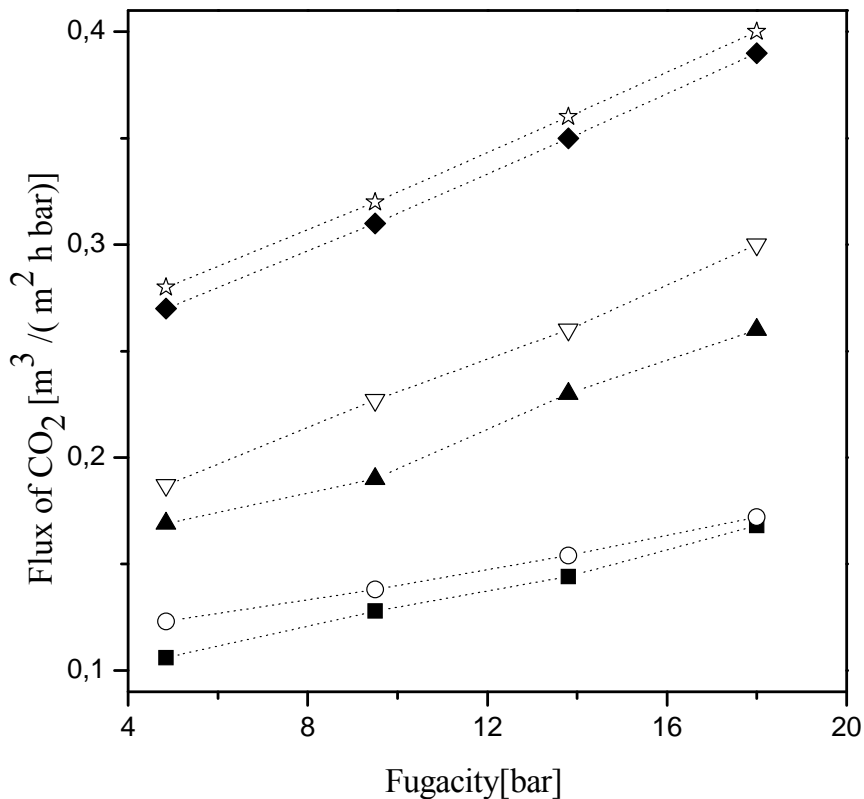


Figure 3: Flux of CO₂ as a function of fugacity in single gas. (■- 0% PEG, ○- 10% PEG, ▲- 20% PEG, ▽- 30% PEG, ◆- 40% PEG and ☆- 50% PEG).

Observing Figure 3, the slope of the line is shifted to higher values with PEG content. Therefore, samples with higher content of PEG show stronger pressure dependence due to the plasticization. The CO₂ sorption levels depend strongly on the segmental packing,

and the plasticization is related to the segmental mobility [30], thus the CO₂ flux at higher operating pressure and high PEG content is always increased.

Single gas transport properties are more often reported than gas mixture data. In most cases pure gas selectivities are lower than mixed gas selectivities, especially when one permeant has a high sorption in the polymer, which causes swelling of the membrane material [31]. However, it is well known that only gas mixture experiments can show and estimate the applicability and feasibility of membranes to separate a target gas mixture.

3.2 Mixed gas measurements

Mixed gas experiments were carried out with 50/50 vol. % in the feed for CO₂/H₂ and CO₂/CH₄, and 25/75 vol. % for CO₂/N₂ at 293 K and a total feed pressure up to 20 bar. The fluxes of CO₂ as a function of the total fugacity are plotted in Figure 4. A pressure increase enhances the CO₂ flux for the CO₂/H₂ and CO₂/CH₄ mixture, which is a consequence of membrane swelling. However, the flux of CO₂ in the CO₂/N₂ mixture slightly decreases with a pressure increase. This behaviour can be attributed to the gas composition in the feed, since high concentration of N₂ would decrease the CO₂ flux due to the plasticization effect, thus the N₂ flux would increase and simultaneously the CO₂/N₂ selectivity is affected, as it will be discussed. It is reported, when a membrane is plasticized by one component from a mixture, the permeability or flux of the other one is increased as well [32]. Stronger plasticization effect could be observed in CO₂/CH₄ mixture (30-50 wt. % of PEG) due to methane presence, since it has stronger sorption behavior than hydrogen and nitrogen. However, all CO₂ fluxes of the membranes measured with mixed gases show good agreement with those obtained by single gas

measurements. Although the CO₂ flux is not significantly increased with the feed pressure, the Pebax[®]/PEG membrane with 50 wt. % of PEG presents high CO₂ flux in the whole operating pressure range (> 0.25 [m³/m²h bar] for CO₂/N₂ mixture). Therefore, Pebax[®]/PEG blend membranes present high performance (high flux) also in mixed gas.

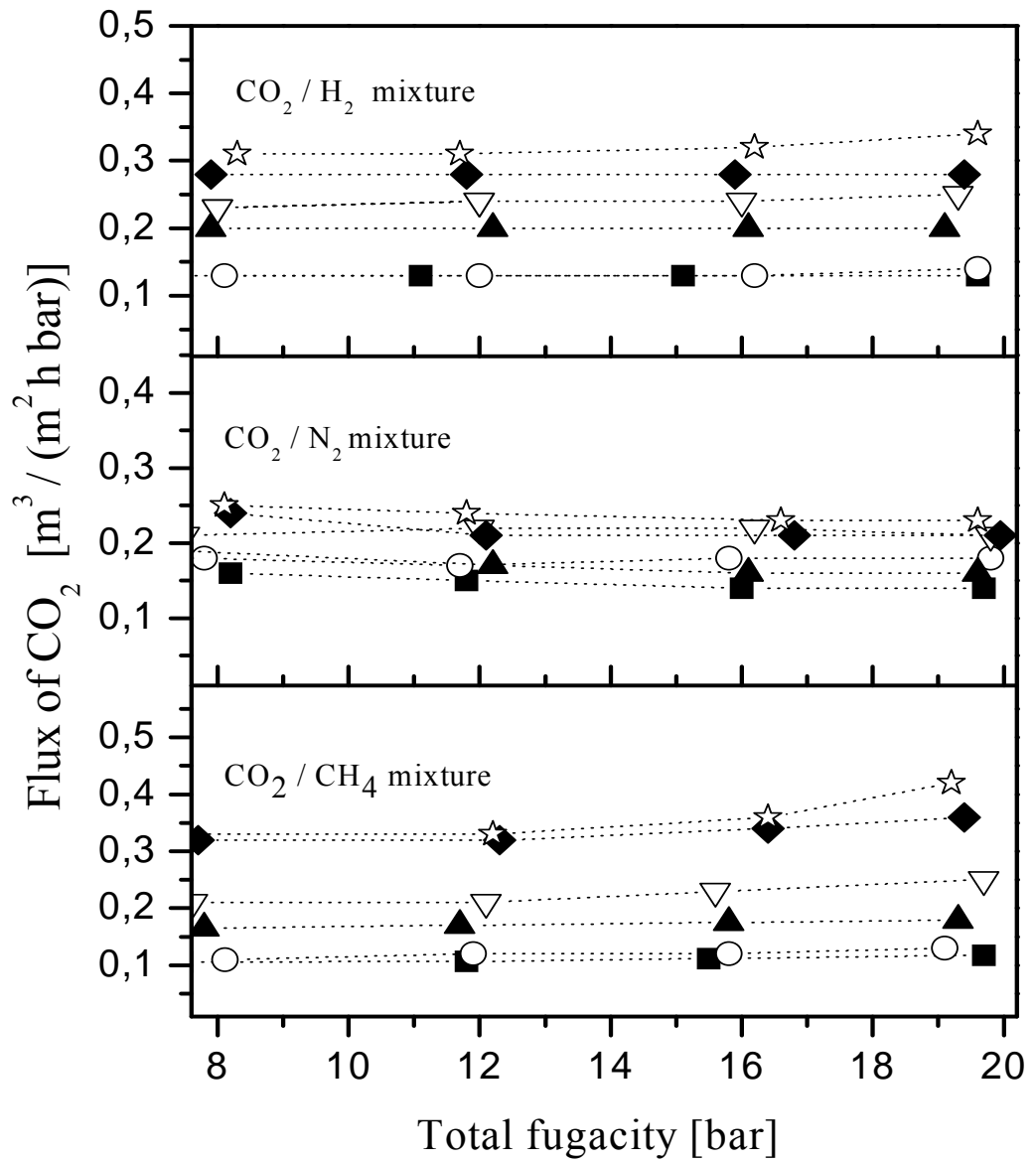


Figure 4: Flux of CO₂ in mixed gas as a function of total fugacity. (-■- 0% PEG, -○- 10% PEG, -▲- 20% PEG, -▽- 30% PEG, -◆- 40% PEG and -☆- 50% PEG).

The selectivity of membranes for mixed gas can be different compared to the selectivity based on single gas [33]. Single gas measurements were carried out from nearly 5 bar with a step of 5 bar, and the mixed gas device allowed to collect reliable data from 7 bar approximately. Although the data are not collected in the same operating pressure for each sample, all results are in the same operating range (see Figure 5). As it is seen, CO₂/gas selectivities based on single gas measurement are higher than mixed gas selectivities due to the plasticization effect.

Membranes with high PEG content present better performance under all operating conditions as shown for single gas. The best improvement in transport properties were obtained for CO₂/H₂ mixed gas (selectivity >9.4 and CO₂ flux >0.31 [m³/m²h bar]). Selectivity is constant for the whole pressure range. This result is in reasonable agreement with that reported earlier for homogeneous films [20]. On the other hand, for CO₂/N₂ mixed gas the selectivity was between 63 and 70 depending on the feed pressure; the CO₂ flux was >0.23 [m³/m²h bar]. The CO₂/CH₄ selectivity for Pebax[®]/PEG blend membranes is similar when compared with pure polymer at 8 bar (around 17), but by increasing the pressure it dropped (~10), which is most evident in blends with higher PEG content (Pebax[®]/PEG with 50 wt. % of PEG). As expected and according to the sorption effects of CO₂ and methane, the high flux (>0.33 [m³/m²h bar]) of CO₂ in this

mixture is accompanied with a flux increase of methane, which leads to lower selectivity in mixed gas.

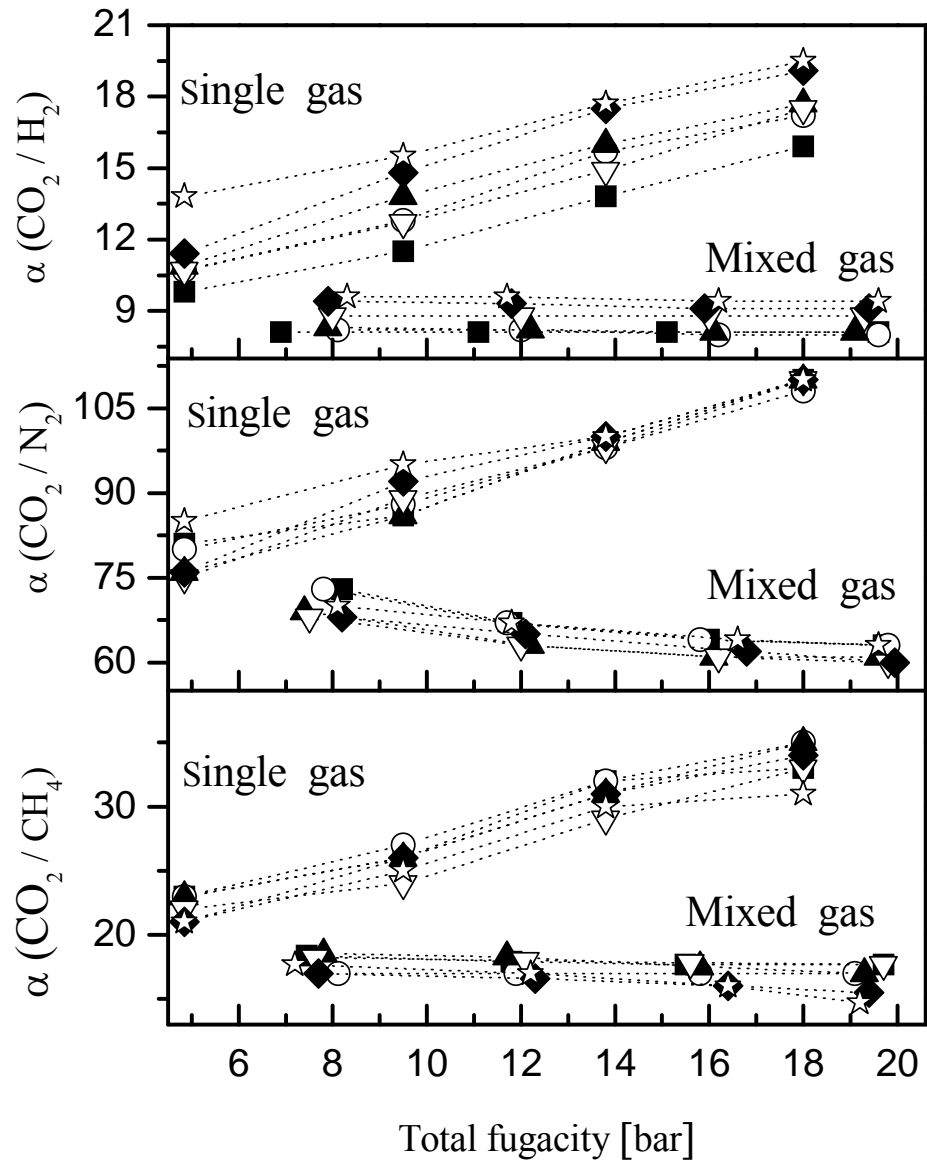
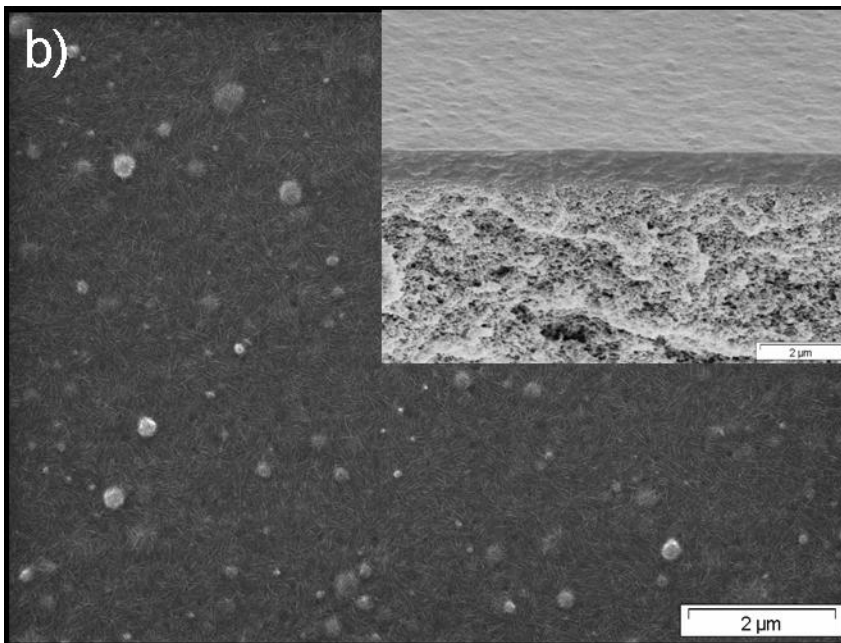
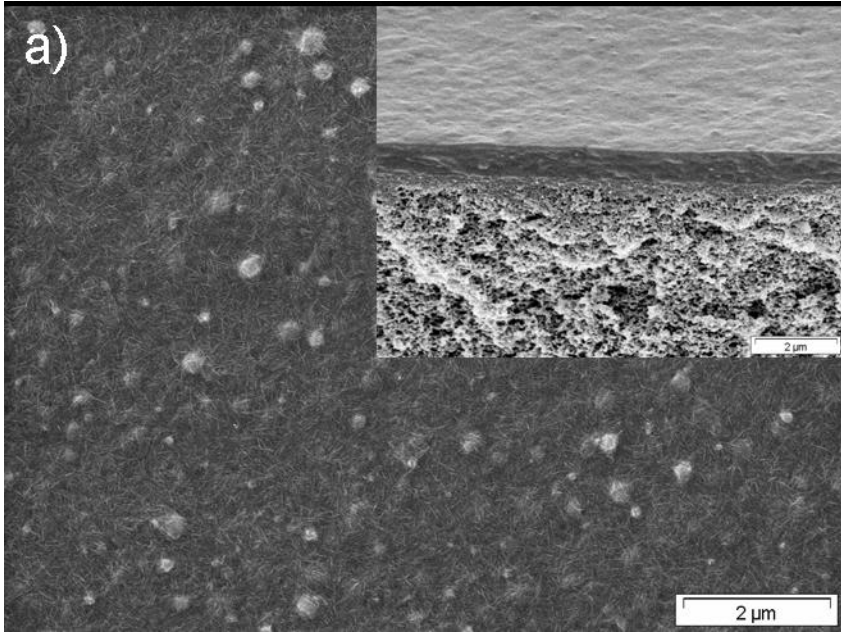


Figure 5: CO₂/gas selectivity in single gas and different mixed gas as a function of fugacity. (-■- 0% PEG, -○- 10% PEG, -▲- 20% PEG, -▽- 30% PEG, -◆- 40% PEG and -☆- 50% PEG.

3.3. Thickness and surface morphology of composite membrane

In order to detect defects on the surface and to estimate the thickness of thin film composite membranes, SEM analyses were carried out with many different samples, but as example only some microphotographs are shown in Figure 6. The thickness of the coating is less than 2 μm, and no-defects were detected. Incorporation of plasticizer induced morphological changes on the membrane surface, as expected. It was reported that PEG (200 g/mol) destroy the lamellar structure of Pebax[®], and consequently the crystallinity decreases with PEG content [20]. The surface of these samples also exhibit a morphology as microphase separated material. This observation is similar to that reported previously. It can be attributed to the preparation method, since the polymer-solvent system is the same.



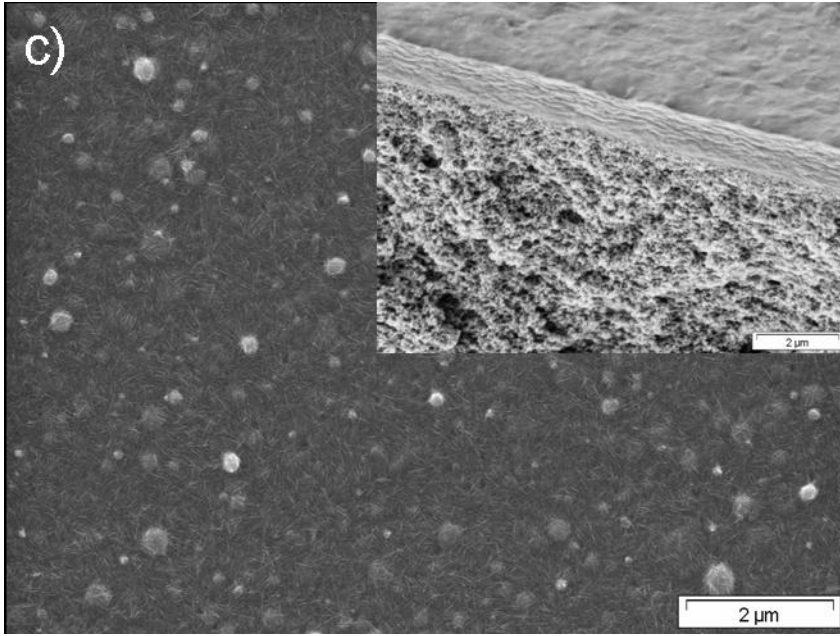


Figure 6: Surface morphology and cross section of the membranes; a) pristine Pebax[®], b) Pebax[®]/PEG with 20 wt. % of PEG, and c) Pebax[®]/PEG with 50 wt. % of PEG.

Conclusion

Pebax[®]/PEG thin film composite membranes were prepared and their ability to separate carbon dioxide from gas mixtures was determined. The effect of operating conditions on performance was investigated. In the temperature range of 283-333 K (single gas at 1 bar) and from 5 to 20 bar (single and mixed gas at 293 K), the CO₂ flux in Pebax[®]/PEG (50 wt. % of PEG) composite membrane was higher than the flux of other samples (Pebax[®], Pebax[®]/PEG with 10, 20, 30 and 40 wt. % of PEG).

The Arrhenius equation was used to calculate the activation energy of diffusion E_D and the heat of sorption H_S for CO₂, H₂, N₂ and CH₄, and it was shown that the PEG presence simultaneously influenced E_D and H_S .

Single gas and mixed gas (CO₂/H₂, CO₂/N₂ and CO₂/CH₄) permeabilities at different total feed pressures were also tested. Single gas experiments showed higher CO₂ flux at higher pressure but in mixed gases the CO₂ flux was almost constant for each binary mixture. Although Pebax[®]/PEG (50 wt. % of PEG) always presented the highest CO₂ flux (single and mixed gas) and high selectivity, the CO₂/CH₄ selectivity in mixed gas slightly dropped compared to pure Pebax[®].

In summary, thin film composite membranes with good performance could be manufactured by using a dilute Pebax/PEG solution in ethanol/water for dip-coating at room temperature. The composite membranes showed exceptional carbon dioxide selectivities and fluxes.

Acknowledgement

The authors thank Karen Prause for the SEM images and Kristian Buhr for calculating the gas fugacities. A. Car thanks the Ministry of Higher Education, Science and Technology, Slovenia and the Deutscher Akademischer Austauschdienst (DAAD) fund for grant.

References

- [1] R. Quadrelli, S. Peterson, The energy climate challenge: Recent trends in CO₂ emission from fuel combustion, *Energy Policy* (2007), article in press.

- [2] By J. Bohannon, Price tags for fighting climate change, ScienceNOW, Daily News, 4 May 2007.
- [3] K. Thambimuthu, J. Davison, M. Gupta, CO₂ capture and reuse, IPCC Workshop on Carbon Dioxide and Storage, Regina, Canada, November 18-21, 2002.
- [4] A. Aspelund, K. Jordal, Gas conditioning-The interface between CO₂ capture and transport, Inter. J. of Green. Gas Control 1 (2007) 343-354.
- [5] J. Davison, K. Thambimuthu, Technologies for capture of carbon dioxide, Proceedings of the Seventh Greenhouse Gas Technology Conference Vancouver, Canada. International Energy Association (IEA), Greenhouse Gas R&D Programme (2004).
- [6] R. W Baker, Membrane Technology and Applications; *McGraw-Hill: New York*, 2000. (pp. 301-392).
- [7] S. Loeb, S. Sourirajan, Sea-water demineralization by means of an osmotic membrane, Adv. Chem. Ser. 38 (1962) 117.
- [8] R. W. Baker, Future directions of membrane gas separation technology, Ind. Eng. Chem. Res. 41 (2002) 1393-1411.

- [9] S.P Nunes, K.-V. Peinemann (Eds.), Membrane Technology in the Chemical Industry, Second, Revised and Extended Edition, Wiley-VCH Verlag GmbH, Germany 2006. (pp. 54)
- [10] H. Lin, B. D. Freeman, Gas solubility, diffusivity and permeability in poly(ethylene oxide), J. of Membr. Sci. 239 (2004) 105-117.
- [11] S. Kulprathipanja, S. S. Kulkarni, Separation of polar gases from non-polar gases, US Patent 4,608 060.
- [12] S. Stern, Polymers for gas separation. The next decade, J. of Membr. Sci. 94 (1994) 1-68.
- [13] L. M. Robeson, Polymer membranes for gas separation, Current. Opi. in Solid State Mater. Sci. 4 (1999) 549-552.
- [14] T. S. Chung, A review of microporous composite polymeric membrane technology for air, Polym. Polym. Composites 4 (1996) 269-283
- [15] V. I Bondar, B. D. Freeman, I. Pinnau, Gas Transport Properties of Poly(ether-b-amide) Segment Block Copolymers, J. Polym. Sci.:Part B: Polym. Physics 38 (2000) 2051-2062.

- [16] J. H. Kim, S. Y. Ha, Y. M. Lee, Gas permeation of poly(amide-6-b-ethylene oxide) copolymer, *J. of Membr. Sci.* 190 (2001) 179-193.
- [17] I. Blume, I. Pinnau, Composite membrane, method of preparation and use, U. S. Patent 4, 963, 165 (1990).
- [18] V. Barbi, S. S. Funari, R. Gehrke, N. Scharnagl, N. Stribeck, SAXS and gas transport in poly(ether-block-polyamide) copolymer membranes, *Macromolecules* 36 (2003) 749-758.
- [19] L. Liu, A. Chakma, X. Feng, CO₂/N₂ separation by poly(ether block amide) thin film hollow fiber composite membranes, *Ind. Eng. Chem. Res.* 44 (2005) 6874-6882.
- [20] A. Car, C. Stropnik, W. Yave, K-V. Peinemann, PEG modified Poly(amide-b-ethylene oxide) Membranes for CO₂ Separation, *J. Membr. Sci.*, (2007), doi:10.1016/j.memsci.2007.09.023
- [21] K. Buhr, Untersuchung neuer Membranmaterialen für Erd- und Raffineriegasanwendungen, Diplomarbeit 2005, Hamburg University of Applied Science.

- [22] J. M. Smith, H. C. Van Ness, M. M. Abbot, Introduction to chemical engineering thermodynamics, McGraw Hill, New York, 2001.
- [23] G. Soave: Equilibrium Constants from a Modified Redlich-Kwong Equation of State, Chem. Eng. Sci. 27 (1972) 1197-1203.
- [24] S. Kelman, H. Lin, E. S. Sanders. B. D. Freeman, CO₂/C₂H₆ separation using solubility selective membranes, J. Membr. Sci., In Press, Corrected Proof.
- [25] R.S. Prabhakar, R. Raharjo, L. G. Toy, H. Lin, B. D. Freeman, Self-consistent model of concentration and temperature dependence of permeability in rubbery polymers, Ind. Eng. Chem. Res. 44 (2005) 1547-1556.
- [26] J. H. Kim, Y. M. Lee, Gas permeation properties of poly(amide-6-b-ethyleneoxide)-silica hybrid membranes, J. Membr. Sci. 193 (2001) 209-225
- [27] H. Lin, E. Wagner, B. D. Freeman, L. G. Toy, R.P. Gupta, Plasticization-enhanced hydrogen purification using polymeric membranes, Science 311 (2006) 639-642.
- [28] H. Lin, E. V. Wagner, R. Raharjo, B. D. Freeman, I. Roman, High-performance polymer for natural-gas sweetening, Adv. Mater. 18 (2006) 39-44.

- [29] H. Lin and B. D. Freeman, Gas and Vapor Solubility in Cross-Linked Poly(ethylene Glycol Diacrylate), *Macromolecules* 38 (2005) 8394-8407.
- [30] L. N Norman., Plasticizing Effect of Permeates on the Selectivity of Polym. *Membr. Eng. Chem. Prod. Res. Dev.*; 1969; 8(3); 281-286.
- [31] M. Wessling, M. L. Lopez, H. Strathman, Accelerated plasticization of thin composite membranes used in gas separation, *Sep. Purif. Technol.* 24 (2001) 223-233.
- [32] T. Visser, G.H. Koops, M. Wessling, On the subtle balance between competitive sorption and plasticization effects in asymmetric hollow fiber gas separation membranes, *J. Membr. Sci.* 252 (2005) 265–277.
- [33] J. Schultz and K. -V. Peinemann, Membranes for separation of higher hydrocarbons from methane, *J. Membr. Sci.* 110 (1996) 37-45
- [34] D. S. Pope, J. W. Koros, Hopfenberg, Sorption and Dilation of Poly(1-(trimethylsilyl)-1-propyne) by Carbon Dioxide and Methane, *Macromolecules* (27) 5839-5844.