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THE APPLICATION OF ZEOLITE NANOPOWDER FOR THE CONSTRUCTION OF THE DENSE COMPOSITE POLYMER MEMBRANES FOR CARBON DIOXIDE SEPARATION

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The main task of the work is to construct the polymeric membrane that could be used for the waste gases treatment. For this purpose, membrane must have high permeability for the carbon dioxide and low permeability of the other gases commonly present in waste gases (hydrogen, oxygen, nitrogen and methane). The constructed membranes were of a dense type, based on a solubility/diffusivity mechanism. In this paper, feasibility of the application of poly(ethyleneoxid)-copoly(phtalamide) was tested. In order to enchase the permeability of carbon dioxide, four different zeolites were added, and in order to improve mechanical stability two different additives were tested. Three zeolites were with the 3-dimensional pores (ZSM5; Faujasite Linde type A) and one was with the 1-dimensional pores (Linde type L). As an additive, n-tetradecyldimethylamonium bromide – n-C14TMABr was tested. The aim of an additive was to provide good wetting of a highly electrically charged zeolite particle by the hydrophobic polymer chains. The other examined additive was dimethylaminopyridine (DMAP) which should improve the solubility of carbon dioxide due to its alkali properties. The best results in carbon dioxide/hydrogen selectivity and permeability were obtained with the membrane constructed with PEBAX 1657 and surface treated zeolite.

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Keywords: Mixed matrix membrane, Zeolite, Carbon dioxide separation, Polymer matrix, Membrane selectivity

1. Introduction

In the recent decades, the global warming appeared as one of the major treatment to the environment, and the carbon dioxide (CO_2). The carbon dioxide is emitted in the atmosphere trough the various processes of combustion, such as industrial energy facilities, power plant facilities, transport and construction. As the fossil fuels currently have no alternative at the global level, great efforts are made in order to reduce the mission of the carbon dioxide. Currently, the main conventional methods for its removal are absorption and cryogenic processes are mainly known [1], [2] and [3]. By the United Nations Framework Convention on Climate Change (UNFCCC, Colloquially known as the Kyoto protocol, the emission of the greenhouse gases has to be reduced by 8% until the end of 2012 [4]. The carbon dioxide separation based on the membranes is suitable in the small and medium scales with moderate requirements concerning the purity of the products. [5]. The interest for the membrane material suitable for the CO2 separation

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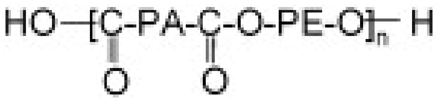
has rapidly increased in last 25 years, and during that time, various polymer materials were examined [6], [7], [8], [9] and [10]. In the recent years [11], ethylene oxide units in the polymer chains have been proved to enhance the solubility of the carbon dioxide, and to achieve high selectivity of carbon dioxide versus other gases. However, the pure poly(ethylene oxide) (PEO) has the strong tendency to crystallize which negatively affects the gas permeability of the membrane[12]. Therefore, the co-polymers that contain EO units can be employed for this purpose. Commercially available polymer under the name PEBAX (supplier Arkema, formerly Atotech) has the structure of poly(amide-b-ether) and can be used as the good alternative material for this purpose [13]. By the properties, PEBAX is thermoplastic elastomere (Fig. 1). As a second choice, the polymer under commercial name Polyactive (supplied by IsoTis OrthoBiologics) was tested (Fig 2.)



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

Fig 1: Structural formula of Pebax co-polymer

PA stands for the polyamide hard block, and usually is nylon-6 or nylon-12, while the PE stands for the soft, amorphous polyether block (polyethylene oxide (PEO) or polytetramethylene oxide (PTMO)) [14].

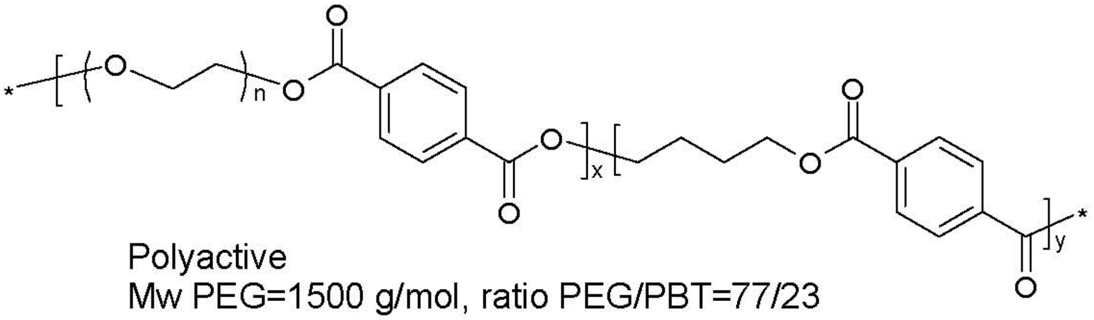


Fig 2: Structural formula of Polyactive co-polymer

As it can be seen from the Fig. 2, Polyactive consists of polyethylene glycol (PEG) and polybutylene terephthalate (PBT). The ratio PEG:PBT is 77:23 (weight %) with PEG of molecular weight of 1500 g/mol

The chemical, physical and mechanical properties of both of the polymers can be easily modelled by the simple variation of the molar ratio of the blocks [16]. Both Pebax and Polyactive have been shown as promising membrane materials for acid gas treatment [17], [18], [19] and [20]. The high selectivity of the carbon dioxide versus nitrogen and hydrogen was reported for the membranes based on those polymers [17]. High selectivity were attributed to the presence of the strong affinity of the ether or ester bonds to the carbon dioxide solution. The high permeability and selectivity of both carbon dioxide and sulphur dioxide versus nitrogen due to the polarizability of gases in the presence of PEO segments was also reported [18]. In order to increase the permeability and selectivity of the membrane, the mixed matrix type of membranes with the inorganic particle and polymer matrix can be constructed. The bulky phase is typically a polymer with the PE block that enhances the solubility of carbon dioxide by itself, and the dispersed phase is inorganic particles [23] and [24]. Those particles can be zeolites, carbon molecular sieves or nanoparticles. The aim of the inorganic filler is to improve the selectivity, permeability comparing to the polymeric membrane due to their inherent separation characteristics. Due to the flexibility of the polymer used as the matrix, fragility as the main problem of the inorganic membrane is avoided.

The first attempts of improvement of the permeability of the mixed matrix membranes was reported 30 years ago, when the diffusion time lag of the carbon dioxide and methane was discovered [25]. Authors have observed that addition of the zeolite increases the time lag, but has apparently no effect on the steady-state permeation. [26].

2. Experimental

The Pebax and Polyactive polymers were supplied by the Arkema and IsoTis OrthoBiologics respectively. The zeolites were supplied by the Institute of Technology of Nuclear and Other Mineral Raw Materials. The zeolites that are used in this research are presented in Table 1. The average specific surface of the zeolite was 500 m²/g.

Table 1. Properties of different types of zeolite used for the construction of the membrane

Type	Framework type code	Channel system, dimension	Pore size, nm
ZSM-5	MFI	3d	0.52 X 0.55
Faujasite	FAU	3d	0.74 X 0.74
Linde Type L	LTL	1d	0.71 X 0.71
Linde Type A	LTA	3d	0.41 X 0.41

Ethanol, chloroform, zeolite, n-tetradecyl trimethylammonium bromide (NTAB) and dimethylaminopyridine (DMAP) were used as received. The aim of the addition of the filler is to provide good contact between the highly charged zeolite particles, and hydrophobic polymer matrix. It was supposed that long, normal chain with the charged end would act as the connector between the two phases. For the DMAP it was also supposed that it would enhance the solubility of the carbon dioxide due to its alkali properties. The Pebax was dissolved in the distilled water/ethanol mixture (70/30 wt.%). The solution (3 wt.% of PEBAX) was stirred for two hours, at the 80°C under reflux. In the case of the Polyactive membranes, the chloroform was used as a solvent, and the solution process was conducted at the room temperature. At the same time, the zeolite particles were dissolved in the same solvent as the polymer, and additive was added (for the samples with the additive). The ultrasound mixture by the titanium head was used for the homogenization. The full power was applied during five minutes, in order to avoid the detachment of the titanium nanoparticles from the head and the contamination of the suspension. This dispersion was poured in the solution of the polymer, and stirred overnight. The stirring temperature for the Pebax membranes was 80°C under reflux, and for the Polyactive membranes room temperature. The long stirring time was needed in order to get as homogenous solution as possible. Viscous solution that came as the result, was casted on the Teflon surface, with the Teflon ring used as the border. The aim of the application of Teflon was to avoid stitching of the membrane to the surface during the drying process. The solution was covered with non-woven textile, and left overnight for the drying at the room temperature and ambient pressure. The drying process had to be slow to avoid the formation of the bubbles which negatively affects the permeation properties of the membrane. If the viscosity of the solution is too high, surface tension dominates the casting process, and the resulting membrane has the uneven thickness. On the other hand, to low value of the viscosity, increases the sedimentation speed of the particles trough the solution of the membrane, and the result is the membrane with non-homogenous dispersion of the zeolite particles trough the volume. If the latter is the case, the membrane self-rolls, and its application is negatively affected. After the drying at the room pressure and temperature was placed on the high vacuum line in order to remove any traces of the residual solvent.

The gas permeability measurements were carried out by the time lag method. The solubility (S), diffusivity (D), permeability (P) and selectivity (α) were determined by the equations[28] and [29]:

$$P = DS = \frac{V_p l (p_{p_2} - p_{p_1})}{ART\Delta t (p_f - (p_{p_2} + p_{p_1})/2)}$$

$$D = \frac{l^2}{6\theta}$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B}$$

In those equations, V_p stands for the constant permeate volume, l for the thickness of the membrane, A for the area of the membrane, R for the universal gas constant, Δt for the time that permeate pressure needs to increase from value p_{p1} to value p_{p2}, p_f for the feed pressure, and θ for the time lag. The solution-diffusion model was used for the analysis of the gas transport properties of the membranes [30]. The selectivity of the membrane for the gas A versus gas B was defined as the ratio of their permeability.

The procedure of the permeability measurements was as follows: After 30 minutes at the high vacuum line, the gas that was measured was applied at the one side of the membrane, while the other side is kept on vacuum. Therefore, the driving force for the diffusion was pressure gradient. The change of the pressure during the time was measured at the vacuum side of the membrane was monitored, and the permeation properties of the membrane were determined by the equations 1-3. The measurements of the gases were done in the following order: hydrogen, nitrogen, oxygen, carbon dioxide. Between measurements of the different gases, the membrane was kept under high vacuum for 15 minutes in order to remove residual gas. The reason for such an order of the gases was to avoid consecutive measurements of flammable gases.

3. Results and discussion

Six different series of the membranes were constructed, three with the each polymer. In the first series, no additive was added, and the membrane was constructed from polymer and zeolite. In the second series, the additive was NTAB, and in the third, DMAP. The composition and the appearance of the membranes are presented in Tables 2., 3. and 4. It should be noted that weight and ratios are calculated as the fraction of the overall weight of the membrane. The compositions of the membranes are compiled in Table 2.

Table 2: The composition and the appearance of the membranes made without the additive

Number of Series	Polymer	Additive
Series I	Pebax	-
Series II	Pebax	NTAB
Series III	Pebax	DMAP
Series IV	Polyactive	-
Series V	Polyactive	NTAB
Series VI	Polyactive	DMAP

The first evaluation was done by the bare eye. Properly made membrane should be transparent, or pale, smooth at the touch, flat and without visible pinholes or damages. Opaque membrane indicates that the contact between the zeolite and polymer chains is not good, and therefore, the light transmits at the polymer-zeolite particle surface. Rough surface indicates uneven distribution of the particles trough the volume of the membrane. Self-rolling of the membrane indicates the sedimentation of the particles, and thus uneven distribution of the zeolite.

The composition and evaluation of the membranes from the series I are given in Table 3.

Table 3: The composition and the appearance of the membranes of the Series I

Membrane Number	Zeolite Filler	Filler, %	Appearance
I-1	FAU	22	white
I-2	FAU	22	white
I-3	FAU	22	white spots
I-4	LTA	22	white
I-5	LTA	22	white areas
I-6	LTL	22	transparent
I-7	ZSM	22	white

From the data presented in Table 3., it is obvious that only the LTL type of the zeolite can be used as the basis for the construction of the further membranes. The contact between the particles of zeolite of FAU, LTA and ZSM type of the zeolite was not good, but construction of the membrane with those fillers and NTAB and DMAP was attempted. White spots on the membrane constructed with FAU came as a consequence of the agglomeration of zeolite particles. Possible reason for this agglomeration is strong electrostatic forces between the particles of the filler that overcome the viscosity of the polymer solution during the drying procedure. Areas of the uneven colour indicate the non-stationary drying process which causes rapid local variations in viscosity of the solution, and therefore, the agglomeration was allowed is some areas of the membrane.

Table 4: The composition and the appearance of the membranes from the Series II

Membrane number	Porous Filler	Filler, %	Additive, %	Appearance
II-1	-	-	3.3	transparent
II-2	FAU	22	3.3	white
II-3	FAU	22	3.3	transparent
II-4	FAU	22	3.3	white areas
II-5	LTA	22	3.3	white spots
II-6	LTL	22.5	2.2	transparent
II-7	LTL	23	1.1	transparent
II-8	ZSM	22	3.3	white

The membrane II-1 was made solely of polymer and detergent additive in order to check their compatibility. As the transparent membrane was yielded, it is reasonable to conclude that this detergent is a promising additive for the compatibillisation. Analyzing the results of the membranes constructed with this additive and other zeolites, it is obvious (Table 4) that only FAU and LTL types of zeolite could be used for the construction of the acceptable membrane. Those results are in the supports the results gained in the experiment of the membrane construction without additive. Those results indicate that the ZSM and LTA zeolites cannot be used for this purpose. In order to check the other possible approach to the zeolite-polymer compatibillisation, the DMAP was used as an additive. It was supposed that although it does not contain long chain and the electrical charge, it still can serve as the compatibilizing additive. It is also supposed that alkali properties of the amine would increase the solubility of the carbon dioxide in the membrane. The results of the attempted membrane construction are compiled in Table 5.

Table 5: The composition and the appearance of the membranes of the Series III

Membrane number	Porous Filler	Filler, %	Additive, %	Appearance
III-1	LTL	21.1	8.5	white
III-2	LTA	21.1	8.5	white
III-3	FAU	21.1	8.5	white
III-4	ZSM-5	21.1	8.5	white

Analyzing the data presented in Table 5., it is obvious that all of the membranes made with DMAP as an additive appeared white, and therefore, the contact between the surface of the particle and polymer matrix was bad. Hence, it might be concluded that DMAP cannot be applied as an additive for the purpose of compatibillisation in this system.

The Polyactive based membranes (Series IV-VI) were constructed in the manner similar to the Pebax ones (Series I-III). The notable difference was that chloroform was used as a solvent instead of the water/ethanol mixture. The application of the chloroform would allow easier removal of the residual solvent from the membrane, due to the hogh volatility of the chloroform. Alternatively, tetrahydrofuran (THF) can be used for this purpose. The amounts of polymer, zeolytes and additives were analogous to the Pebax based membranes. The composition and evaluation are presented in Table 6.

Table 6: The composition and the appearance of the membranes of the Series IV

Membrane number	Porous Filler	Filler, %	Appearance
IV-1	-	-	Transparent
IV-2	LTA	22	Transparent
IV-3	LTA	22	Transparent
IV-4	LTA	32	white spots
IV-5	FAU	22	white spots
IV-6	FAU	22	white spots
IV-7	LTL	22	Transparent
IV-8	LTL	22	Transparent
IV-9	ZSM	22	White

The Sample IV-1 was constructed from the pure Polyactive in order to compare the properties of the pure polymer to the literature data. The results obtained in the experiment were slightly different from the specification. This difference might be attributed to the different batch of the polymer, or eventually the error in the measurement. The samples IV-2 and IV-3 were made with LTA zeolyte, and the firs evaluation have given the good results. However, when the increase in the concentration of the zeolyte was attempted (Sample IV-4), the agglomeration occurred, and the white spots became visible. Similarly to the Pebax based membranes (Series I), the LTL has been proved to be a good additive, resulting in the smooth, transparent membrane (Samples IV-7 and IV-8). The Samples IV-5 and IV-6 (constructed with FAU) resulted in the membrane that contain white spots on the surface. Although it can appear similar to the case of Pebax based membranes, the agglomeration is present in this case, instead of the bad surface contact in the case of Pebax. This implies the different nature of the surface behaviour of the same zeolyte in when dispersed in the same polymer. The application of ZSM zeolyte resulted in the white, non-transparent membrane in both of cases (Samples I-7 and IV-9). Therefore, it was decided to include ZSM during the construction of the membranes with NTAB as an additive (Series V). The composition of the membranes and their evaluation is presented in Table 7.

Table 7: The composition and the appearance of the membranes from the Series V

Membrane number	Porous Filler	Filler, %	Appearance
V-1	-	-	Transparent
V-2	LTA	22	white areas
V-3	LTA	22	white areas
V-4	FAU	22	white spots
V-5	LTL	22	Transparent
V-6	LTL	22	Transparent
V-7	ZSM	22	White

Based on the observation of the Sample V-1, it can be seen that the NTAB itself does not agglomerate, and therefore it can be used as an additive. Nevertheless, similarly to the analogous Pebax membranes, only the LTL resulted in a transparent and smooth membrane. The addition of the NTAB to the LTA type of zeolyte (Samples V-2 and V-3) results in the formation of white areas on the membrane. This might be the consequence of excess of the zeolyte, so not all the particles might be covered. However, if the amount of the additive is further increased, the precipitation of the zeolyte occurs. The reason for the precipitation is similar to the reason for the agglomeration, and can be attributed to the electrostatic forces. The presence of the additive does not influence the appearance of the membranes constructed with FAU and ZSM zeolytes (V-4 and V-7 respectively). The sample V-4 shows strong agglomeration of the inorganic filler, while the sample V-7 provides no contact between the zeolyte particles and polymer. Their behaviour is analogous to the behaviour of samples constructed without the additive (samples IV-5, IV-6 and IV-9).

The membranes based on the Polyactive were also constructed with the DMAP as an additive in order to test the possibility of enhancement the solubility of carbon dioxide. The gained results are presented in Table 8.

Table 8: The composition and the appearance of the membranes of the Series III

Membrane number	Porous Filler	Filler, %	Additive2, %	Appearance
VI-1	LTA	21	8.5	White
VI-2	FAU	21	8.5	White
VI-3	LTL	21	8.5	rolled
VI-4	ZSM	21	8.5	-

As it is obvious from the Table 8, no applicable membrane was made with the DMAP as an additive. The membranes with LTA and FAU (samples VI-1 and VI-2 respectively) provided no good contact between the zeolyte and polymer. In the case of the LTL (Sample VI-3), the zeolyte that has shown the best results in previous systems, the rapid sedimentation occurred, and the membrane was rough at the one side and rolled due to the uneven distribution of particles. In the case of the ZSM (Sample VI-4), drying resulted in the powder, rather than the membrane. Based on the outcome of membranes with the DMAP as the additive (Series III and VI), it is reasonable to conclude that the DMAP cannot be used for the compatibilizataion of Pebax and Polyactive membranes.

Prior to the measurement of the membranes, permeability of samples II-1 and V-1 were measured. The reason was to determine weather the addition of the NTAB affects the permeability of pure polymer. The outcome of the measurements clearly indicates that there is no change in the permeability of the pure polymer when the NTAB is dispersed.

For the measurements of the gas permeability and the selectivity, only smooth and transparent membranes were chosen. This includes membranes with LTL and FAU (Pebax) and membrane with LTL (Polyactive). The Polyactive based membrane with LTA and LTL without NTAB were measured as well.

The results of permeability and selectivity measurements are compiled in Table 9.

Table 9: The results of the permeability measurement of the membranes

Membrane number	Thickness, μm	P (CO_2), Barrer	α (CO_2/H_2)	α (CO_2/O_2)	α (CO_2/N_2)
II-3	252	88	9.1	23	48
II-6	174	128	9.7	22	55
II-7	150	131	9.4	20	52
IV-2	217	142	11.8	23.5	62.4
IV-3	191	139	10.9	21.7	60.4
IV-7	121	130	9.2	20.9	54.7
IV-8	162	135	9.5	21.1	54.8
V-5	232	142	11.6	22.0	61.1
V-6	199	137	11.3	21.7	60.5

It should be noted that the usual unit for the gas permeability of the membrane in the membrane research community is Barrer. One Barrer is the permeability of 1 cm^3 of a gas under the standard pressure and temperature conditions, trough the 1 cm2 of the area and 1 cm of the thickness driven by the pressure gradient of 1 cmHg in 1 s divided by the factor of 10^{-10}.

Analyzing the permeability data presented in the Table 9, it is obvious that all of the membranes that appeared transparent have shown good and comparable permeability and diffusivity properties. The best results regarding the permeability and selectivity were gained by the dispersion of the LTA type of the zeolyte in the Polyactive. The results were good for both surface treated and non-treated zeolyte. The dispersion of the LTL in the Polyactive resulted in the membrane with the comparable permeability and selectivity, but with the 20%-30% of the thickness reduction. Concerning the Pebax based membranes, FAU and LTL yielded acceptable results, with the permeability and selectivity comparable to the Polyactive based membranes.

4. Conclusion

In this paper, the possibility of the construction of the mixed matrix membrane based on the polymer matrix and surface treated inorganic powder was examined. The membranes were constructed with two different types of polymer, four different zeolites, and two different additives. The optical testing has shown that not all of the combinations are suitable for the construction of the membrane. Concerning the membranes based on Pebax, only LTL and FAU types of zeolites are compatible with both surface treatment reagent and polymer. In the case of the

ZSM and LTA types of zeolite, good contact between the particles and polymer chains could not be provided. In the case of the Polyactive based membranes, only untreated LTL and LTA could be used. The NTAB has been shown to be good additive that does not negatively influence the properties of the membranes. On the contrary, DMAP did not yielded acceptable results. The permeability of the polymer membrane filled with the zeolite increased by approximately the factor of 2, with the retaining the selectivity of the membrane. Therefore, in may be concluded that mentioned polymer-zeolites combinations and NTAB as an additive are promising base for the future research. However, the downsizing of the thickness of the membrane will be the main challenge for the future work. As the main application of those membranes is planned to be in the wet conditions, the next step in this research would be to measure the selectivity and permeability of the zeolite-filled membranes in the wet conditions.

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References

[1] A.B. Rao and E.S. Rubin, Environ. Sci. Technol., **36,** 4467–4475 (2002).
[2] U. Desideri and R. Corbelli, Energy Convers. Manage., **39,** 857–867 (1998).
[3] A. Meisen and S. Xiaoshan, Energy Convers. Manage., **38,** 37 (1997).
[4] The United Nations Framework Convention on Climate Change, Kyoto, 1997
[5] W.J. Koros and G.K. Fleming, Membrane-based gas separation. J. Membr. Sci., **83,** 1–80 (1993).
[6] S.P. Nunes, K.-V. Peinemann, Editors, Membrane Technology in the Chemical Industry, (second revised and extended edition), Wiley-VCH Verlag GmbH, Germany (2006), pp. 53–150
[7] K. Ghosal and B.D. Freeman, Gas separation using polymer membranes: an overview. Polym. Adv. Technol., **5,** 673 (1994).
[8] R.W. Baker, Membrane Technology and Applications, McGraw-Hill, New York (2000), pp. 301–392.
[9] R.W. Baker, Future directions of membrane gas separation technology. Ind. Eng. Chem. Res., **41,** 1393 (2002).
[10] P. Yu, Yampol'skii, I. Pinnau and B.D. Freeman, Materials Science of membranes, John Wiley& Sons, England (2006), pp. 1–47
[11] H. Lin, B.D. Freeman, Materials selection guidelines for membranes that remove CO_2 from gas mixtures. J. Mol. Struct., **739,** 57 (2005).
[12] H. Lin and B.D. Freeman, Gas solubility diffusivity permeability in poly(ethylene oxide). J. Membr. Sci., **239,** 105 (2004).
[13] L.A. Utracki, History of commercial polymer alloys and blends, Polym. Eng. Sci., **35,** 2 (1995).
[14] G. Deleens, N.R. Legge, G. Holder, H.E. Schroeder, Editors , Thermoplastic Elastomers: A Comprehensive Review, Hanser Publishers, New York (1987), pp. 215–230
[16] M. Yoshino, K. Ito, H. Kita and K.-I. Okamoto, Effect of hard-segment polymers on CO_2/N_2 gas separation properties of poly(ethylene oxide)-segmented copolymers. J. Polym. Sci. Part B Polym. Phys., **38,** 1707 (2000).
[17] V. Bondar, B.D. Freeman, I. Pinnau and Gas Sorption, Characterization of poly(ether-b-amide) segmented block copolymers. J. Polym. Sci. Part B Polym. Phys. **37,** 2463 (1999).
[18] J.H. Kim, S.Y. Ha and Y.M. Lee, Gas permeation of poly(amide-6-b-ethylene oxide) copolymer. J. Membr. Sci., **190,** 179 (2001).
[23] A. Car, C. Stropnik, W. Yave, K.-V. Peinemann, PEG modified poly(amide-b-ethylene oxide) membranes for CO_2 separation, Journal of Membrane Science, **307**(1), 88 (2008).
[24] A. Car, C. Stropnik, W. Yave, K.-V. Peinemann, Tailor-made Polymeric Membranes based on Segmented Block Copolymers for CO2 Separation, Advanced Functional Materials,

18(18), 2815 (2008).

[25] D.R. Paul and D.R. Kemp, The diffusion time lag in polymer membranes containing adsorptive fillers. J Polym Sci: Polym Phys, **41,** 79 (1973).
[26] Kulprathipanja S, Neuzil RW, Li NN. Separation of fluids by means of mixed matrix membranes. US patent 4740219, 1988
[28] A.M. Shishatskii, Y.P. Yampolski and K.-V. Peinemann, Effects of film thickness on density and gas permeation parameters of glassy polymers. J. Membr. Sci., **112,** 275 (1996).
[29] J. Qiu, J.-M. Zheng and K.-V. Peinemann, Gas transport properties of poly(trimethylsilylpropyne) and ethylcellulose filled with different molecular weight trimethylsilylsaccharides: impact on fractional free volume and chain mobility. Macromolecules, **40,** 3213 (2007).
[30] G. Wijmans and R.W. Baker, The solution–diffusion model: a review. J. Membr. Sci., **107,** 1 (1995).