Gas Separation Properties of the Dense Polymer —Zeolite Powder Composite Membranes

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The natural balance in the Earth's atmosphere is significantly influenced by the human emission of the combustion products, mainly carbon dioxide. Therefore, strong efforts are directed in the direction of the reduction of that emission. The solution might be searched in the direction of the construction of the membrane that would be highly transparent to the carbon dioxide, but not transparent to the other gases commonly present in the waste gases (oxygen, nitrogen, hydrogen, methane). One of the feasible designs for this purpose is dense, non-porous membranes, with zeolite particles dispersed in the polymer matrix. Zeolite particles should increase the solubility of the carbon dioxide, and thus enhance its permeability. In this paper, the possibility of application of polyether-b-amide (with 60% of PEG) as a polymer matrix was tested. For the inorganic component, four different zeolite types with three different pore geometries were tested. The influence of the additive which was added in order to provide good contact between the highly polar and charged zeolite inorganic particle, and hydrophobic polymer chains was also tested.   [doi:10.2320/matertrans.M2015387]

1. Introduction

High emission of the carbon dioxide and other waste gases in the past decades has faced mankind with the great concerns in the environmental engineering. Increased concentration of carbon dioxide in atmosphere is responsible for both greenhouse effect, and the acid rains. Carbon dioxide emission mainly comes from the combustion processes at the industrial as well as the communal scale (heating plants, power plants, different procedures in chemical industry, automobile engines).[1,2] As demand for the energy increase every day, and the fossil fuels have no feasible alternative on the world-scale, importance of carbon dioxide removal from the waste gases has become one of the emergencies of the present-day environmental engineering.[3,4]

Possible approach to carbon dioxide capture is the implementation of membrane that would separate carbon dioxide from rest of the gases. Suitable membrane should exhibit high permeability for the carbon dioxide, and the lowest possible permeability for the other gases. Standard (porous) membranes are not suitable for this purpose as the separation should be done at the molecular level.[5,6] Standard membranes use the difference in the eluent particle size, which is not applicable in this case, as the diameter of carbon-dioxide molecule is significantly larger than the hydrogen or oxygen molecule.[7] Therefore, so-called dense, non-porous membranes based on the solution-diffusion mechanism must be employed. Mechanism of separation for those membranes is that the effluent is adsorbed on the surface on the membrane, and then is dissolved in the matrix of the membrane, and then diffuses through the thickness of the membrane layer.[8–10] 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.[11] The negative aspect of the application of 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. PA can be composed of various polyamides (nylon-6 or nylon-12), while the PE stands for the soft, amorphous polyether block (polyethylene oxide or polytetramethylene oxide).[14] The hard polyamide block serves as the mechanical carrier of the membrane, while the PE phase is responsible for the diffusion.[15] The chemical, physical and mechanical properties of the polymer can be easily modeled by the simple variation of the molar ratio of the blocks.[16] Pebax® has been shown as promising membrane materials for acid gas treatment.[17–20]

As the first approximation, theoretical comparison of molecular properties of carbon dioxide versus other gasses (especially hydrogen) shows that carbon dioxide molecule is significantly bigger. Therefore, the hydrogen diffuses much faster as its molecule is small and non-polar and, hence, has higher diffusivity coefficient. Therefore, the solubility of the carbon dioxide must be increased in order to obtain good selectivity for the carbon dioxide versus hydrogen. Analogous situation is in the case of nitrogen and oxygen molecules, but the difference in diffusivity is not so high as their molecules are bigger than hydrogen's, and thus, the diffusion coefficients are lower. However, the solubility of oxygen and nitrogen should be kept as low as possible.[21–25]

In order to prepare proper film for the casting of the membrane, the zeolites have to be dispersed in the same solvent as the polymer. Crucial step in this procedure is to provide good wetting of the zeolite particles by the polymer chain. This task can be extremely tedious as the inorganic zeolite particles are highly polar and hydrophile, and show very bad affinity to the highly hydrophobe polymer chains. In addition, proper film must be free of any pin holes, with the

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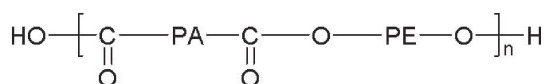*Corresponding author, E-mail: dragutin@tmf.bg.ac.rs

Fig. 1   Structure of the PEBAX 1657 used as a matrix.

Table 1   Properties of the zeolites used in experiment.

Type	Channel system	Pore size, pm	Max. diff. diam., pm
CFI	1d	75	73
OWE	2d	58	38
IWS	3d	82	67
ITR	3d	64	57

homogenous distribution of zeolite particles in the polymer matrix. To fulfill this task, different additives can be added. The aim of the additive addition to the matrix is to act as a compatibilizer between the zeolite particles and polymer matrix.

2.   Materials and Methods

For the research in this paper, possibility of application of polyether-b-amide with 60% of PEG was investigated. This polymer has shown good mechanical and diffusion properties for this purpose. This polymer is available under the commercial name PEBAX 1657 from the supplier Arkema. The structure of this polymer is presented on Fig. 1.

Inorganic nanopowder (zeolite) was dispersed in the polymer matrix in order to enhance the solubility of carbon dioxide. The properties of the zeolite can be described at the macro and microlevel. At the macrolevel, the properties of the powder are determined by the specific surface of the particles. Particles used for the experiments presented in this paper have the specific surface of 500–900 m^2/g. On the microlevel, properties of the zeolite are determined by the directions of the pores and the maximum sphere diameter that can diffuse along it. For this experiment, four different zeolite types with three different pores geometries were used.

The zeolite of CFI pore type is composed solely from silicon and oxygen (Si32O64), and posses 1-dimensional pores with 73 pm as the maximal diameter of sphere that can diffuse along it. The zeolite of OWE type is 2-dimensional zeolite with max. diffusion diameter of 59 pm. IWS and ITR are both 3-dimensional zeolites with maximal diffusion diameter of 121 and 119 pm respectively. All of the mentioned structures are selected due to their relatively high diffusion diameters that should enhance the diffusion of large carbon dioxide molecule. Properties of the zeolite powders are compiled in Table 1.

Those crystal lattices act as sieves at the molecular level. The molecular schemes of the zeolites are presented on Figs. 2–5. The zeolite powders were supplied by the company NanoScape, and characterization was done by the supplier.

As the additive, n-tetradecane trimethyl ammonium bromide (n-C14-TMABr) was tested. The aim of this additive is to provide good contact between zeolite nanoparticles and polymer matrix. The supposed mechanism is that the polar nitrogen—bromine bond would "attach" to the surface of the zeolite particle, and the long, normal, hydrocarbon tale would act as an "anchor" to the polymer matrix. It was supposed that the compactibility between the zeolite and polymer would be achieved by this mechanism. Presumed mechanism of those interactions is presented on a Fig. 6.

The procedure for the construction of the membrane was as following: The PEBAX 1657 was dissolved in the water/ethanol mixture (30/70 vol% respectively). The dissolution
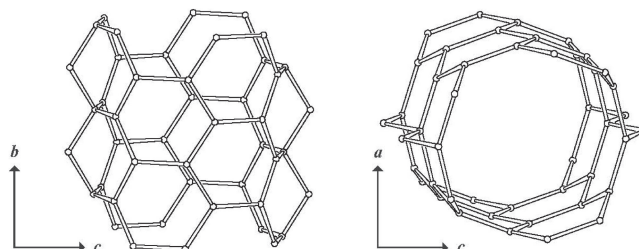

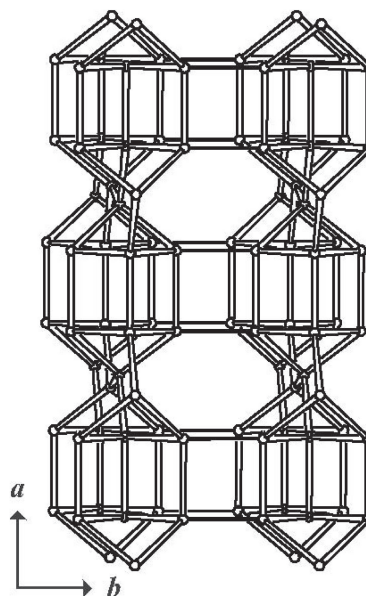Fig. 2   Structure of the CFI zeolite.

Fig. 3   Structure of the OWE zeolite.

was done at the 80°C under reflux for 15 minutes. The zeolite was dispersed in the small amount of the same mixture, and (eventually) additive was added. The amount of zeolite dissolved was calculated versus amount of polymer. Ultrasound mixer was used as it provides good and homogenous dispersion. The titanium head was positioned in the solution, and the mixing was done by ultrasound frequency of 40 kHz with the power of the source of 90 W. The mixing time was relatively short because if the full power is applied for the longer time, nano particles of titanium are detached from the ultrasound head, and released in the solution causing the contamination. This dispersion was mixed with the solution of polymer and stirred overnight at the 80°C under reflux. Viscous solution that came as a result was casted on the Teflon surface with the Teflon ring used as a border. This solution was covered with non-woven textile, and left overnight for drying at the ambient pressure and the room temperature. The drying process had not to be faster, as air bubbles might be formed in the volume of the membrane, and
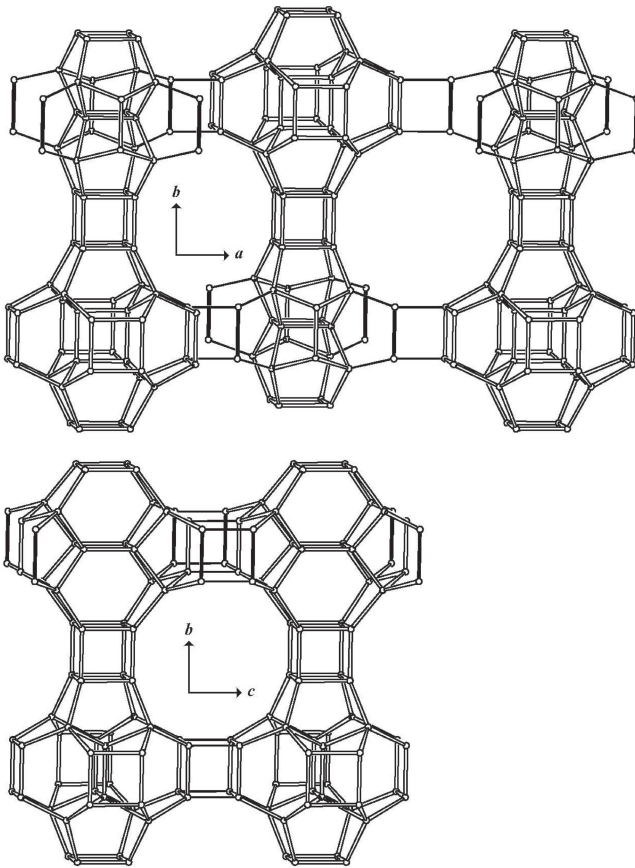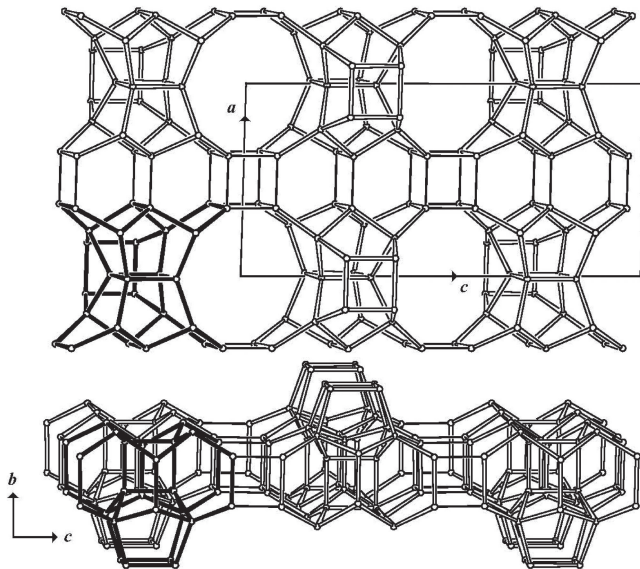
Fig. 4 Structure of the IWS zeolite.

Fig. 5 Structure of the ITR zeolite.

membrane cannot be used for the gas separation. At this level it, is extremely important to obtain the polymer solution with the optimal viscosity. If the viscosity is too high, the surface tension dominates trough the casting of the membrane, and the result is the membrane with the uneven thickness, which negatively affects the overall permeation properties of the membrane. On the contrary, too low value for the viscosity causes the sedimentation of the zeolite particles, and the zeolite is concentrated on the one side of the membrane.
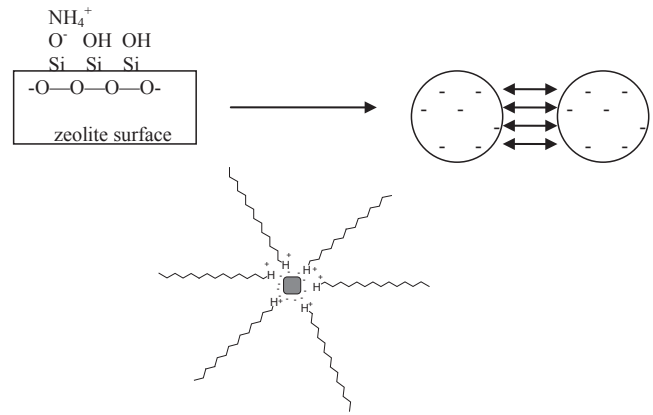

Fig. 6 Presumed mechanism of compatibilization of zeolite particles and polymer matrix with n-C14-TMABr.

If the latter is the case, the membrane self-rolls, and its application is negatively affected. After the drying at the ambient pressure and temperature, membrane was placed in the apparatus for the permeability measurements, and put at the vacuum (pressure under 250 Pa) in order to remove any residual of the 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:[26,27]

$$P = DS = \frac{V_p l (p_{p2} - p_{p1})}{A R T \Delta t \left(p_f - \frac{(p_{p1} + p_{p2})}{2} \right)} \quad (1)$$

$$D = \frac{l^2}{6\Theta} \quad (2)$$

$$\alpha_{(A/B)} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \quad (3)$$

In those equations, V_p stands for the constant permeate volume [cm^3], l for the thickness of the membrane [cm], A for the area of the membrane [cm^2], R for the universal gas constant [J/K mol], Δt for the time that permeate pressure needs to increase from value p_{p1} to value p_{p2} [s], p_f for the feed pressure [mm Hg], and θ for the time lag [s]. The solution-diffusion model was used for the analysis of the gas transport properties of the membranes.[28] The selectivity of the membrane for the gas A versus gas B was defined as the ratio of their permeability. Analyzing the eqs. (1)–(3), it is obvious that both solubility and diffusivity of the gases must be taken into account in order to define properties of the suitable membrane.

The equipment for the measurements of the permeabilities is presented at the Fig. 7. The permeability measurements were done by the application of the gas at the one side of the membrane, with the vacuum ($p < 50$ Pa) applied at the opposite side at the start of the measurement. This difference in pressure acted as a driving force for the gas diffusion. Gases were measured one at the time and in order to remove any residual gas that was solved in the membrane, vacuum (under 50 Pa) was applied between the measurement of the different gases. The permeabilities of hydrogen, oxygen, nitrogen, methane and carbon dioxide were measured, and all the selectivities were calculated versus carbon dioxide. The
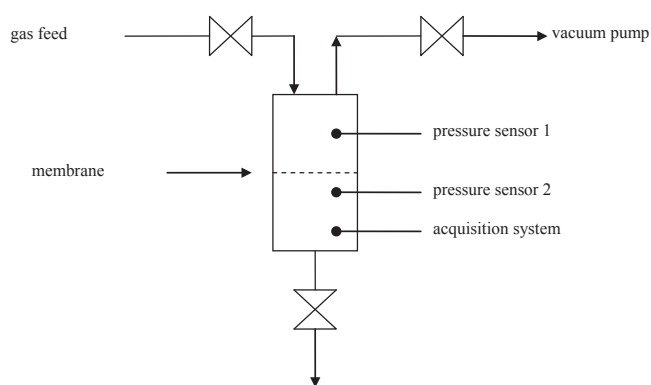
Fig. 7 The equipment for the measurements of the permeabilities for the dense polymer-zeolite composite membranes.

Table 2 The composition and optical appearances of the constructed membranes.

Membrane number	Porous Filler	Filler, %	Additive	Additive %	Appearance
1	—	—	—	—	transparent
2	—	—	n-C14-TMABr	—	transparent
3	CFI	22.3	—	—	white
4	CFI	22	n-C14-TMABr	8.6	opaque
5	OWE	22.3			white spots
6	OWE	21.9	n-C14-TMABr	8.5	opaque
7	IWS	22	—	—	white
8	IWS	21.8	n-C14-TMABr	8.5	transparent
9	ITR	22	—	—	opaque
10	ITR	22.5	n-C14-TMABr	8.3	transparent

Table 3 Permeability and selectivity of the constructed membranes.

Membrane number	Thickness, μm	P CO_2, Barrer	α (CO_2/H_2)	α (CO_2/O_2)	α (CO_2/N_2)
4	192	110	8.5	20.9	62.2
6	241	122	7.9	21.0	54.9
8	185	125	8.9	20.8	62.8
9	192	121	9.1	20.7	60.5
10	221	125	8.8	20.6	60.0

permeability of helium was also measured for the determination weather membrane contain pin hole or not. The gases were used as received from the supplier.

3. Results and Discussion

The compositions and physical appearances of the constructed membranes are compiled in Table 2. All the presented percent were mass percent versus polymer. The permeabilities of the membranes that contained white spots or white areas were not measured. As it is stated in the introduction, white spots indicates aggregations of the zeolite particles, and thus implies non-uniformous distribution of particles, and thus, bad permeation properties. The agglomeration further implies that most of the zeolite particles were not covered with the additive and that the adhesive forces between the zeolite particles prevail in the system. The white color of the membrane implies the bad contact between the zeolite particles and polymer chains. If the air gap is present, the light refraction occurs in the gap, and the membrane appears white. Membranes that appeared white were not measured as well, as white color indicates bad contact between the surface of the zeolite and the surface of the polymer. Opaque membranes might have those gaps as well. However, their opacity implies that most of the particles are in good contact with the polymers, and that "air gapping" appears only at the small fraction of the particles. The first two samples were made in order to check the possibility and feasibility of making the membrane of the pure polymer as well as the behavior of the additive dispersed in the pure polymer. As the gained results were successful in the matter of thickness and the appearance of the membrane, this system was used for the construction of the membranes with polymers.

Analyzing the appearance of the various membranes, it can be seen that addition of the n-C14-TMABr rapidly improves the appearance of the membrane. In the ideal case, the membrane should appear transparent, smooth, without any visible spots or zones of the different color. This appearance implies that the inorganic particles are evenly distributed trough the membrane, and that contact between the polymer and inorganic particles is good. In the previous experiments with the similar polymer—zeolite systems, no statistical relation between the opacity and the permeability of the

membranes were observed. Therefore, only opaque and transparent membranes were used for the permeability measurements.

The results of the permeability and selectivity measurements are presented in Table 3. The permeability is expressed in the units of Barrer which is common among the membranes research. The permeability of one Barrer is the permeation of 1 cm^3 of oxygen through 1 cm thick membrane with the area of 1 cm^2 with the pressure difference of 1 mm Hg during one second times 10^{-10}. Ratio to the corresponding SI unit is that 1 Barrer is equivalent to 3.35×10^{-16} m^3/m^2 Pasm.

As it can be observed from the Table 3, all of the membranes with good appearance have shown good permeability and selectivity. The permeability of the carbon dioxide was around 120 Barrer which is lower, but still comparable with other similar systems (the difference does not exceed 10%). Selectivity of the carbon dioxide versus hydrogen was just under 9 while the values for oxygen and nitrogen were over 20 and 60 respectively. Comparing the values for the permeability of the membrane made of the zeolite with different pore systems it can also be observed that 3-dimensional systems (membranes 9 and 10) have shown slightly better result in comparison with 1- or 2-dimensional systems. Possible explanation might be that in 1-dimensional system (and partly in 2-dimensional) orientation of the pores plays significant role in the diffusion of the gas molecules through the membrane. If the pore of the 1-dimensional zeolite system is the perpendicular do the direction of the diffusion, the possible path of the diffusing molecule is longer, and therefore diffusion is slower. The control of the orientation of the pores is possible, however, that would

made the membrane preparation procedure longer and more demanding. The slight decrease in the selectivity between the membranes 9 and 10 might be attributed to the presence of the additive, which enhances diffusivity of both carbon dioxide and hydrogen.

The main task of the future research efforts is to reduce the thickness of the membrane. In order to test membranes in the conditions that are as similar as the real exploitation, the other direction for the research would be testing of the performance of the membrane at the wet conditions and with several gases simultaneously.

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 tested. The constructed membranes are dense, mixed-matrix membranes. The membranes were constructed with polyether-b-amide with 60% of PEG as a matrix and one of the four different zeolite particles as the dispersed inorganic phase. As an additive, the n-tetradecane trimethyl ammonium bromide (n-C14-TMABr) was tested. By the observation of the membranes after their construction, it was concluded that the presence of the C14-TMABr provides better contact between the polymer chains and zeolyte particles. Therefore, the gaps at the contact surface are avoided which improves overall separation performance of the membrane. The membrane with the acceptable quality could not be achieved without the addition of the C14-TMABr. The obtained permeability of the carbon dioxide, and the membranes' selectivity of carbon dioxide versus hydrogen (as the main research interest of the experiments) were 120 Barrer and approximately 9, respectively. Those values are slightly lower in comparison with other systems. The permeability of the membranes constructed with 3-dimensionals zeolite pores are slightly higher in comparison with analogous 1- and 2-dimensional systems. One of the possible reasons for that could be that the orientation of the pores play significant role in the permeability of the membrane.

Acknowledgement

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