

The Influence of Polymer Concentration and Formation Technique on Gas Transport and Gas Sorption Properties of Copolyetherimide-Based Composite Membranes Containing MIL-101 Filler

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Abstract—Composite mixed-matrix membranes for gas separation containing copolyetherimide Siltem[®] as the polymer matrix and metal-organic framework MIL-101 (10 wt %) as the active filler, were obtained using dry and wet-dry formation techniques. It has been found that the polymer concentration in the initial solution does not significantly affect the CO₂ and CH₄ permeability of the film membranes obtained by dry molding. The addition of MIL-101 CO₂/CH₄ increases the selectivity of the dry-formed membranes approximately by 2 times compared to the selectivity of the filler-free polymer membranes. The materials synthesized by the wet-dry formation possess increased permeability and inverted CO₂/CH₄ selectivity, which indicates a change in the gas transport mechanism. With the increase of polymer concentration, the selectivity of the membranes obtained by the wet-dry technique, increases significantly due to the formation of the dense selective layer.

Keywords: composite membranes, gas separation, morphology, gas transport properties, gas sorption properties, permeability

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INTRODUCTION

Methane conversion is one of the most important reactions in chemical technology. The separation of methane from carbon dioxide plays a crucial role in this process. The membrane gas separation method is suitable for this purpose. It has several advantages such as low energy intensity, environmental friendliness, low cost and simplicity of use [1]. Nowadays polymer membranes are most widely used but they possess low chemical and thermal stability. Besides, there is a fundamental trade-off between their gas transport properties: materials with high permeability have low gas separation selectivity, and vice versa [2, 3]. To overcome these restrictions, mixed-matrix membranes (MMMs) consisting of a polymer and an inorganic disperse filler can be employed [4, 5].

The filler addition to a polymer solution is the most widespread method of making MMMs [6, 7]. However, the influence of polymer concentration in the molding solution remains insufficiently explored. As it was shown in [8, 9], permeability of polysulfone-based materials with respect to water solutions decreases up to 80% due to the structure densification with the increase of the polymer concentration from 17 to 30%.

Such studies on membrane gas separation, including MMMs, have not been carried out yet.

The aim of this work is to determine the influence of the polymer concentration in the molding solution and the formation technique on gas transport and gas sorption properties of gas separation film membranes based on silicon-containing copolyetherimide Siltem[®] and metal-organic framework MIL-101 as a filler.

MATERIALS AND METHODS

Copolyetherimide Siltem[®] is a soluble amorphous thermoplastic [10] in the form of polymer granules with glass transition temperature of 148°C (Fig. 1). Aromatic polyetherimides are one of the most promising types of membrane polymers due to high gas separation selectivity [11], and the modification of these materials with organosilicon fragments leads to the certain permeability increase [12].

Metal-organic frameworks (MOFs) are a new class of highly porous solid compounds, which consist of metal ions or inorganic clusters connected by polydentate organic ligands [13]. Among the MOFs, mesoporous chrome(III) terephthalate MIL-101(Cr) is one of the most promising fillers for mixed-matrix

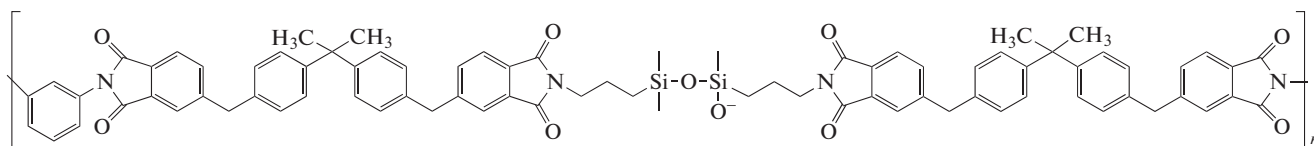


Fig. 1. The structural formula of Siltem[®] copolyetherimide.

membranes. This material with specific surface area of 4200 m²/g has high thermal and chemical stability and can selectively adsorb up to 50 mmol/g of carbon dioxide [15]. In this work, the MIL-101 samples produced by the classical hydrothermal technique [16] were used.

To prepare molding solutions, Siltem[®] granules were dissolved in N-methyl-2-pyrrolidone with stirring for 6 h. The series of solutions with polymer concentration of 20.0; 22.5; 25.0; 27.5 and 30.0 wt % was obtained. Then the calculated amount of MIL-101 (10% of the polymer mass) was added to the solutions. For uniform distribution of the filler particles, the dispersion of MIL-101 in Siltem[®] solution was treated for 30 min in a UZD-3,5 ultrasonic generator with submersible emitter ("Kriamid", Russia).

To obtain the membrane films with adjusted thickness, the dispersion of MIL-101 in the polymer solution was evenly distributed on a glass support by an applicator. After that, the molding by two different techniques was carried out.

(1) Dry formation. The solvent evaporation was conducted on air [7]. The membrane preforms were heated in a ShSV-65 IZ drying cabinet ("Teplopribor", Russia) at 100°C during 3 h with subsequent cooling at room temperature.

(2) Wet-dry formation. The preform was placed into a coagulation bath filled with water [7]. The coagulation process occurring faster near the film surface resulted in formation of a prominent anisotropic structure with a large number of small pores.

After the molding, the film samples obtained by dry and wet-dry techniques were kept in water for 48 h to remove the residual solvent, and then were dried on air. The thickness of produced membranes was determined by a micrometer.

The morphology of the membranes was studied by scanning electron microscopy (SEM) on a Tescan Vega 3 microscope (Czech Republic). To make the SEM images of membrane brittle fractures, the films were preliminarily frozen in liquid nitrogen.

Gas transport properties of the obtained membranes were determined using a barometric installation GKSS (Germany) with the integral mode of gas flux registration [17]. The permeability measurements were carried out at 25°C and under the initial gas pressure of 1 bar. The LabView software was used for processing of the results.

Gas sorption properties of the film membranes were determined with a volumetric Sieverts-type apparatus [16]. The membrane samples were put into a stainless steel autoclave and degassed for 5 h at 25°C in vacuum of 10⁻² mbar. To determine the void volume of the measuring system, the preliminary calibration with helium was applied. All measurements of the excess adsorption capacity were carried out at 25°C and 20 bar. Three measurements were done for each sample and each gas, and later the average values were calculated. The gas density values under different pressures were taken from NIST database (USA) [18].

RESULTS AND DISCUSSION

Structure and Morphology

The morphology of the membranes was studied by SEM. According to the obtained images, the film samples produced by the dry technique from 25.0 wt % polymer solution have more homogenous structure than the samples synthesized from 22.5 and 30.0 wt % solutions (Fig. 2). Such differences in morphology can be explained based on the Flory–Huggins polymer solution theory [19]. According to this theory, at low concentrations the statistical coils of the polymer are separated by solvent molecules. The excess of a certain concentration limit leads to the overlapping of the coils. In these extreme cases, the films with uneven and highly defective structure are formed.

The membranes made by the wet-dry formation have different morphology (Fig. 3). In this case, the formed porous anisotropic structure is mainly determined by the conditions of the polymer coagulation in the precipitant (water), and not by the distribution of polymer statistical coils during the solvent evaporation. According to the SEM data, in the sample obtained from 22.5 wt % solution the polymer forms the uneven porous structure with many defects. The gas transport study of the sample was not possible because of its insufficient mechanical durability. At higher concentrations of the coagulating solution, the bottle-type channels, through which the solvent is diffused into the coagulation bath, are formed.

For the film membranes produced by the wet-dry formation from 27.5–30.0 wt % polymer solutions, the structure of bottle-type channels changes insignificantly. However, at the surface of the film samples obtained from the 30.0 wt % solution a new denser layer is formed. This selective and non-porous layer,

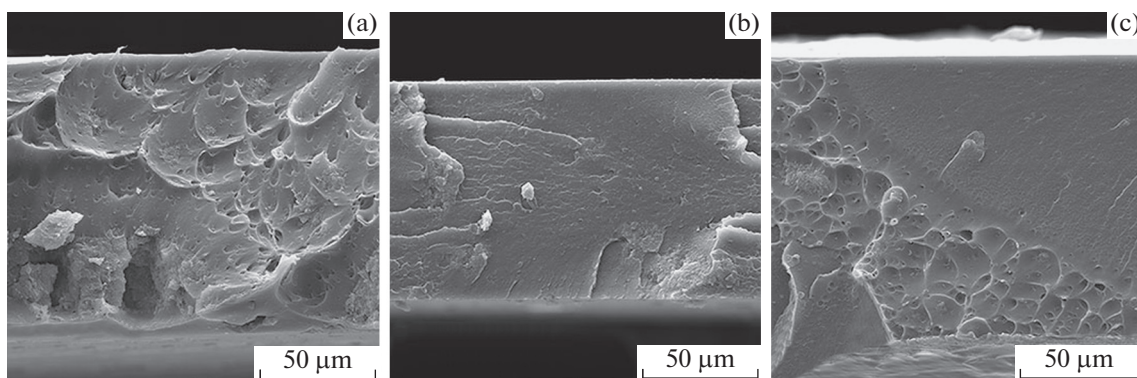


Fig. 2. SEM images of brittle fracture of Siltem[®] – MIL-101 membrane films obtained by dry formation. The concentration of the polymer in the initial solution (wt %): (a) 22.5, (b) 25.0, (c) 30.0.

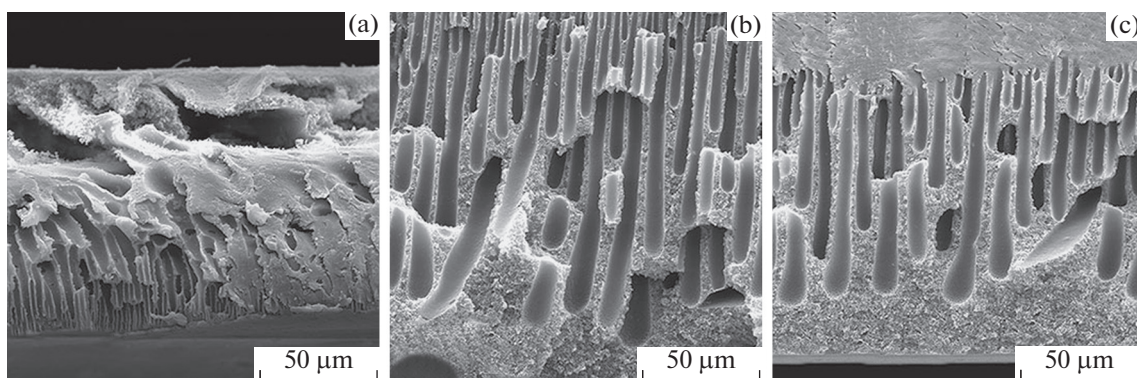


Fig. 3. SEM images of brittle fracture of Siltem[®] – MIL-101 membrane films obtained by wet-dry formation. The concentration of the polymer in the initial solution (wt %): (a) 22.5, (b) 27.5, (c) 30.0.

which blocks the openings of the channels, has the structure similar to the films obtained by the dry technique. It allows to decrease the permeability and to increase the gas separation selectivity.

Gas Transport Properties

Permeability with respect to carbon dioxide and methane (that is the stationary gas flux, which passes thorough the membrane of known area and thickness) was calculated by the integral Daynes–Barrer method [20] using the experimental gas pressure values as a function of time:

$$P = (J_{\infty}l)/(\Delta pA),$$

J_{∞} – stationary gas flux, Δp – pressure difference on both sides of the membrane, l – membrane thickness, A – membrane area.

Ideal selectivity was calculated as the ratio of permeabilities for two different gases:

$$\alpha_{A/B} = P_A/P_B,$$

$\alpha_{A/B}$ – ideal separation selectivity for A and B gases, P_A and P_B – permeabilities for A and B gases, respectively.

The experimental data on gas permeability of studied film membranes are presented in Table 1 (the properties of MIL-101-free films are included for comparison). As seen from Table 1, the films produced by the dry formation possess higher CO₂ permeability compared to CH₄. The polar imide groups of Siltem[®] provide more efficient transport of polar carbon dioxide molecules than of non-polar methane molecules.

The permeability of the membranes made by the dry technique with respect to both gases decreases with the polymer concentration increase from 22.5 to 25.0 wt %. The further concentration rise up to 30.0% wt. leads to the permeability increment. This pattern is observed for both plain Siltem[®] membranes and composite samples containing MIL-101. It can be related to the membrane structure defectiveness that reduces within the concentration range of 22.5 to 25.0 wt % but increases again at higher concentrations. The afore-

Table 1. Permeability (P) and CO_2/CH_4 separation selectivity (α) of Siltem® + 10% MIL-101(Cr) film membranes obtained by dry and wet-dry formation techniques

MIL-101 concentration in the film	Siltem® concentration in the molding solution, wt %	Dry formation			Wet-dry formation		
		P , Barrer		$\alpha_{\text{CO}_2/\text{CH}_4}$	P , Barrer		$\alpha_{\text{CO}_2/\text{CH}_4}$
		CO_2	CH_4		CO_2	CH_4	
No filler	22.5	75	28	2.7	100 000	150 000	0.7
	25.0	56	19	2.9	370 000	530 000	0.7
	27.5	66	20	3.3	350 000	470 000	0.7
	30.0	75	25	3.0	100 000	150 000	0.7
10 wt %	22.5	98	23	4.4	—	—	—
	25.0	74	16	4.6	360 000	500 000	0.7
	27.5	89	20	4.6	340 000	480 000	0.7
	30.0	95	23	4.1	3000	1000	3.0

mentioned permeability changes are insignificant and almost do not affect the membrane selectivity.

The addition of 10 wt % MIL-101 to the membranes produced by the dry formation increases the CO_2 permeability by 1.3 times and slightly decreases the CH_4 permeability. As a result, the selectivity of the mixed-matrix membranes is significantly higher.

The permeability of the samples synthesized by the wet-dry technique is 10^2 – 10^4 times higher than the permeability of the materials prepared by the dry technique (Table 1). This fact can be explained by differences in the film morphology: the dry technique allows forming dense structures (Fig. 2) while the wet-dry technique leads to porous structures (Fig. 3) which provide higher permeability.

There are no significant permeability changes after the addition of MIL-101. The ideal CO_2/CH_4 selectivity of the films obtained by the wet-dry technique from 25.0–27.5 wt % solutions appears to be inverted (0.7). This means that gas transport in these films occurs due to viscous flow through wide canals [7]: the permeability is determined by size of gas molecules and not by their interaction with the polymer or the filler.

With the concentration increase from 27.5 to 30.0 wt %, the permeability abruptly decreases by 2 orders of magnitude with the simultaneous selectivity increase from 0.7 to 3. This is close to the values obtained for the samples made by the dry technique (approximately 4–5). This fact is related to the formation of an asymmetrical selective layer at the membrane surface (Fig. 3c). There is a gas transport change to solution-diffusion mechanism, which is specific for films obtained by the dry technique. It should be noted that such an effect was not observed for the MIL-101-free wet-dry films made from 30 wt % solution. The formation of denser and more ordered structure in the absence of the filler crystal particles is impeded.

Gas Sorption Properties

The solution-diffusion mechanism is the basic principle of gas transport in non-porous polymer membranes. It consists of the penetrant molecule solution in the bulk of the membrane and the consequent diffusion under the action of external concentration gradient [7]. To evaluate the influence of the disperse filler and polymer concentration in the molding solution on sorption interactions with the studied gases, additional volumetric experiments were performed. As results of these measurements, the excess sorption capacities (q_{ex}) with respect to carbon dioxide and methane were calculated. These values correspond to the excess amount of gas in solid phase compared to the “film sample – helium” reference system, where adsorption interaction is negligible. The calculations were done using the following formula:

$$q_{\text{ex}} (\text{mmol/g}) = \frac{n_{\text{g}}}{m_{\text{sorb}}} = \frac{p_1 V_1 - p_2 V_2}{m_{\text{sorb}} M_{\text{g}}},$$

n_{g} – adsorbed gas amount, m_{sorb} – sorbent mass, p_1 and V_1 – gas density and gas-occupied volume before the measurements, p_2 and V_2 – gas density and gas-occupied volume upon reaching the equilibrium, M_{g} – gas molecular mass.

According to Table 2, the excess adsorption of carbon dioxide and methane in the film samples obtained by the wet-dry technique is higher than in the membranes produced by the dry technique. This is due to the formation of porous channeled structure during coagulation. With the increase of polymer concentration in the cast solution, the sorption capacity remains approximately the same. Therefore, the influence of morphology on excess adsorption is insignificant. These patterns are true for both plain polymer membranes and mixed-matrix composites.

It has been established that the presence of 10 wt % MIL-101 in film samples almost does not affect the

Table 2. Excess adsorption capacity of Siltem® + 10% MIL-101(Cr) film membranes obtained by dry and wet-dry formation techniques

MIL-101 concentration	Siltem® concentration in the molding solution, wt %	q_{ex} , mmol/g			
		dry formation		wet-dry formation	
		CO ₂	CH ₄	CO ₂	CH ₄
No filler	22.5	1.4	0.4	1.6	0.4
	25.0	1.1	0.4	1.7	0.4
	27.5	1.1	0.3	1.7	0.4
	30.0	1.2	0.3	1.5	0.3
10 wt %	22.5	1.3	0.3	1.6	0.3
	25.0	1.1	0.3	1.8	0.4
	27.5	1.1	0.4	1.7	0.4
	30.0	1.2	0.3	1.6	0.5

CO₂ and CH₄ excess adsorption capacities for both dry and wet-dry techniques. It is known that excess sorption capacity of this MOF at 30°C and under 20 bar equals 20 mmol/g with respect to CO₂ and 6 mmol/g with respect to CH₄ [15]. This means an expected increase of adsorption by 2.0 and 0.6 mmol/g, respectively, in recount for MIL-101 loading in a Siltem®-based membrane.

However, the given data show that there is no improvement of adsorption capacity for both dry and wet-dry formation techniques. This fact clearly indicates the suppression of MOF sorption activity in the film membranes that is connected to the conditions of the composite membrane synthesis from a polymer solution. As we have shown in [21], the passivation of hydrophilic porous fillers (such as MIL-101) during the membrane formation from polymer solution can be caused by pore blocking by adsorbed solvent molecules. Taking into account the sorption values reported in [21] and related to the filler treated in N-methyl-2-pyrrolidone, we conclude that the improvement of sorption capacity at the addition of MIL-101 is insignificant within the margin of error.

Thereby, the MOF does not manifest its gas sorption ability in the film membranes and the changes of gas transport parameters in the presence of the filler are determined by its influence on morphology of the composite material containing interphase boundaries.

CONCLUSIONS

(1) The selectivity of CO₂/CH₄ gas separation by film membranes based on copolyetherimide Siltem® and made by the dry formation technique almost does not depend on the polymer concentration in the molding solution. The addition of 10% Cr-MIL-101 increases their selectivity by 1.6 times. The membranes obtained by the wet-dry formation from 25.0–27.5% polymer solutions possess higher permeability and inverted CO₂/CH₄ selectivity. This can be explained by gas transport through wide channels in form of vis-

cous flow. In the composite membrane made from 30% Siltem® solution, the dense selective layer is formed that changes the gas transport mechanism to “solution-diffusion”. Herewith the selectivity value specific for the dry-formed samples is reached.

(2) The volumetric studies of CO₂ and CH₄ sorption indicate that the addition of MIL-101 to the polymer matrix does not lead to expected increase of gas sorption ability of composite membrane materials. Such behavior can be caused by the blockage of the metal-organic filler pores by solvent molecules adsorbed during the film membrane formation process. The influence of MIL-101 on gas transport properties of Siltem®-based membranes is determined primarily by morphology changes on interface between the polymer and the disperse filler, and not by sorption activity of the added filler.

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CONFLICT OF INTEREST

There is no conflict of interest.

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