



Gas transport through mixed matrix membranes composed of polysulfone and copper terephthalate particles

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ABSTRACT

In this work gas transport and structural investigations of heterogeneous membranes composed of polysulfone and copper terephthalate (CuTPA) particles are reported. Three types of CuTPA, varying in surface area, pore volume and pore size distribution, as it was shown by nitrogen physisorption, were investigated as membrane fillers. Structural characterization of pure CuTPA and composite membranes was carried out by positron annihilation lifetime spectroscopy, calorimetry, derivatography, electron microscopy, X-ray diffraction and density measurements. CuTPA possessing high porosity was found to increase permeability of heterogeneous membranes to N₂, O₂, He, CO₂. In contrast, permeability decrease was observed for two other types of CuTPA with lower porosity. Additionally, membranes containing highly porous CuTPA were annealed at two different temperatures and it was found that higher temperature results in higher both membrane permeability and selectivity. For example, CO₂ permeability for membrane annealed at 150 °C was 1.65-times higher than that for pure PSF, whereas membrane annealed at 200 °C was 3.3-times more permeable. This significant change in membrane permeability was ascribed to residual solvent removal from CuTPA pores.

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1. Introduction

Copper terephthalate is a transition metal complex, which belongs to the metal-organic frameworks (MOFs), crystalline solids composed of metal ions interconnected by organic linkers. MOFs are a unique class of the so-called tailored porous materials. Although crystalline arrangement resulting in porous character is a feature common also for other, conventional porous materials like zeolites, there are a few properties, which differentiate MOFs from them. Firstly, many of MOFs reveal very high surface areas allowing for adsorption of substantial amounts of gases or organic vapors [1–3]. Secondly, there is a broad possibility to tune MOFs properties by using various inorganic cations and organic linkers, which allow for obtainment of desired pore sizes and geometries as well as for incorporation of specific chemical groups into structure [4]. Therefore, MOFs have attracted the highest scientific and industrial attention with applications being focused on gas adsorption and

storage [5], catalysis [6] as well as membrane separation [7]. MOFs have also been investigated as components of mixed-matrix membranes (MMMs). MMMs, in their simplest form, are two-component systems, in which particles of component A are dispersed in a continuum matrix of component B. Usually, component B is a polymer material, because of its easy processability and appropriate mechanical properties, whereas particles A are typically made of inorganic or metal-organic materials. Particles A could be either impermeable or permeable to the given substance. The effect of permeable, porous particles on transport in MMM results from sorption and diffusion of transported substances inside particles pores as well as from changes in polymer matrix properties, which may take place due to the presence of the particles. The interest in MOFs as fillers of heterogeneous membranes results not only from their diverse and tunable porosity but also from their superior to zeolites compatibility with polymers [8–10]. Because separation properties of many porous materials are not well-recognized, many works in the MMM field have been aimed at finding correlations between MMM permeability and these filler properties, which are expected to influence its

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permeability [11]. Such filler properties comprise: pore size and its distribution, pore volume and topology, chemical composition of particles surface and pore wall. Pore limiting diameter, i. e. diameter of the largest sphere that can pass through a pore window, is the most often considered property. For example, it was shown that the incorporation of fillers with a pore limiting diameter close to dimensions of transported molecules, increased membrane selectivity towards small gases [12–15]. However, it was also reported that for a highly selective filler, selectivity of MMM could remain unchanged if permeabilities of both MMM components are very different [16].

Although there are examples in the literature that MOF-containing membranes reveal excellent performance, the physical phenomena governing gas transport in such membranes are still not fully recognized. For example, incorporation of ZIF-8 into different polymers always resulted in a permeability increase, however selectivity changes were different; selectivity was found to increase for some matrices [12,17,18] and to stay constant or to reveal non-monotonous behavior for others [19,13]. As it was stated in recent review by Yampolskii et al. [9], such differences seem to be the result of effects taking place at the interface rather than of penetrant sorption and diffusion in the ZIF-8 pores.

Copper terephthalate consists of Cu^{II} dimers interconnected by benzenedicarboxylate anions confined within a specific crystallographic plane [20]. Layers, created in this way, tend to stack together due to weak interactions between them [21]. Porous character of CuTPA, allowing for the adsorption of a substantial amount of gases, was confirmed for the first time by Mori et al. [22,23]. Recently, Carson et al. presented the crystal structure of two forms of copper terephthalate: solvated by DMF molecules ($\text{CuTPA} \cdot \text{DMF}$) [21] and after desolvation [24]. In $\text{CuTPA} \cdot \text{DMF}$, each Cu atom coordinates one DMF molecule in a vertical position relative to terephthalate ligands. DMF molecules can be removed from material by heat treatment at temperatures much above 200 °C or by extraction with methanol followed by drying at 160 °C [24]. The desolvation process leads to the material of a different crystal structure, possessing a linear pores system (Fig. 1) in which the largest diameter is almost the same as the limiting

diameter and equals to 5.2 Å. Additionally, after desolvation, Cu atoms are coordinatively unsaturated and therefore they reveal Lewis acid character.

To the authors knowledge, up to now there were three reports on mixed-matrix membranes containing CuTPA particles. Adams et al. investigated membranes containing 15, 30 and 50 wt% of CuTPA in poly(vinyl acetate) (PVAc) matrix [25,26]. They showed that membranes with the highest CuTPA content are about four times more permeable than PVAc. Interestingly, the smaller was the gas, the larger was the permeability increase. However, this relationship did not hold for helium, for which permeability enhancement was nearly the same as for carbon dioxide, although the former is significantly smaller than the latter (2.6 Å vs 3.3 Å of kinetic diameter). Rodenas et al. compared effect of CuTPA nanosheets, revealing aspect ratios above 20, with that of isometric CuTPA particles on CO_2/CH_4 mixture separation properties of poly(ether imide)-based membranes [20]. The authors reported that incorporation of both material types resulted in CO_2 permeability decrease. However, membranes containing CuTPA nanosheets were significantly more selective than both pure poly(ether imide) and MMM containing isometric particles. The authors attributed this result to more effective filling of MMM cross-section (perpendicular to gas flow) by nanosheets, compared to isometric particles, which results in a larger amount of gas molecules being transported through nanosheets than through the pure matrix. However, as the authors admitted, the synthesis and activation procedure they adopted did not allow for the removal of DMF molecules from the material pores. This was reflected in very low BET surface areas presented by them for nanosheets ($53 \text{ m}^2 \text{ g}^{-1}$) and isometric particles ($11 \text{ m}^2 \text{ g}^{-1}$) suggesting a lack of micropores in those materials. Feijani et al. investigated CuTPA-containing membranes based on PVDF, a rubbery semicrystalline polymer [27]. They found a monotonous increase in carbon dioxide and helium permeability. For membranes containing 15 wt% CuTPA, the increase for CO_2 was more than two-fold, for He about 1.4-fold. In contrast, changes of N_2 and CH_4 permeabilities were less than 10%.

Hence, in view of the results of the presented studies, the application of CuTPA as a filler in other MMMs merits investigation. The aim of the present contribution was threefold: i) to discover whether CuTPA filler is able to improve permeability and/or selectivity of polysulfone – a polymer widely used in industrial membrane gas separations, ii) to investigate the effect of the filler porosity on MMMs performance and iii) to get some insight into the phenomena influencing gas transport in PSF/CuTPA heterogeneous membranes. Different types of copper terephthalate, varying in BET surface area, pore volume and micropore volume, were investigated as fillers. Additionally, the effect of annealing temperature on the MMMs transport properties was also studied and shown to be significant.

2. Experimental

2.1. Materials

Copper nitrate trihydrate (min. 99%) was purchased from Chempur (Poland) and terephthalic acid (min. 98%) from Aldrich. Solvents: N,N-dimethylformamide (DMF, 99.8%), methanol (99.8%) and chloroform (98.5%) were obtained from POCH (Poland). All chemicals were used as received. The water content, given by the manufacturer, was below 0.05% in each chemical. Polysulfone powder (Udel) was kindly delivered by Solvay Advanced Polymers. Purity of gases, which transport was tested, was as follows: for oxygen 99.95% and for the rest of the gases at least 99.995%; they were all purchased from Messer Polska.

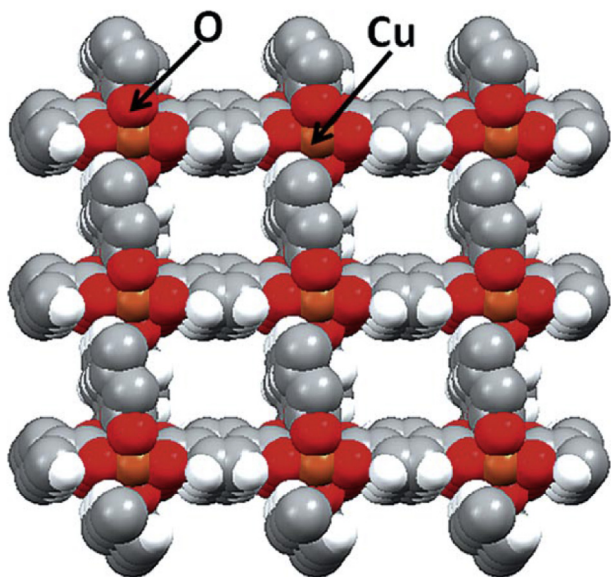


Fig. 1. Desolvated CuTPA framework viewed down the a axis, obtained from work by Carson et al. [24] with permission from John Wiley and Sons.

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