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Detailed investigation on laboratory scale mixed-matrix-membrane preparation for gas separation

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Introduction

The key parameters for gas separation are the permeability and the selectivity. In early 1990s Robeson plotted permeability versus selectivity of a specific gas pair and graphically showed that unfortunately performance of polymeric membranes has an upper limit [1]. In order to enhance separation properties of existing membranes and to exceed the Robeson upper-bound limit, researchers started to developed mixed matrix membranes (MMMs) [2]. MMMs are expected to overcome these limitations by merging of organic polymer and inorganic particle phases. Inorganic materials with their unique pore structure having molecular sieving ability, surface chemistry and mechanical strength provide an attractive improvement of separation properties [3, 4].

Many of these researches resulted in improved performances of prepared MMMs compared to polymer membranes and gave hope to pass over the Robeson upper bound limit. However, some other researchers found worse performances as a reason of different difficulties which might be encountered in preparation of MMMs [5].

Aim of the work

Producing of MMMs has difficulties such as poor particle distribution, weak contact of particles in the polymer matrix, or inconvenient filler-polymer combination [5]. Among numerous studies, limited research has been focused specifically on producing MMMs for gas separation. The aim of this work is to develop a reliable procedure for preparation of reproducible and defect-free laboratory-scale MMMs.

Additionally, within the scope of the project, V. Kramer has developed a mechanistic model for mass transfer of selected gases in MMMs. One of the most important assumptions of the model is that pores of filler particles are not filled up with the polymer. In the concept of producing MMMs, a detailed investigation to avoid pore blockage is examined.

Experimental

Producing sorption selective MMMs requires a careful material selection. In this work polydimethylsiloxane (PDMS) was selected as continuous phase and porous carbon adsorbent produced by the Blücher GmbH was chosen as dispersed filler phase.

Producing MMMs consists of four fundamental steps: (1) preparation of membrane materials; as polymer solution and pretreatment of inorganic filler, (2) mixing polymer solution and filler, (3) casting these mixture onto a support structure to form a MMM film, and (4) drying of prepared MMMs as a post-treatment step.

Polymer precursor solution was diluted with solvent and then mixed with cross-linking agent and catalyst as described by the producer. Parameters like type of stirrer, mixing time, and mixing rate has been identified to get a homogenous mixture. Storage conditions of the final PDMS solution have been investigated.

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The crucial point in the first step is pretreatment of carbon particles. Carbon particles were dried in a vacuum oven at 100 mbar and 150°C for 12 hours to avoid any adsorbed components. However, one of the major difficulties encountered in preparation of MMMs is pore blockage of carbon particles resulting in low selectivity. To overcome this defect, carbon particles have been saturated with a solvent before mixing with PDMS. In order to determine pore blockage quantitatively Energy-Dispersive X-ray Spectroscopy (EDX) analysis was applied to the cross section area of carbon particles.

The procedure of the producing MMMs is continued with preparing a homogeneous solution of polymer and particles. For this purpose, different methods were tested. Mixed-matrix layer was coated on the support structure. As a final step, drying conditions of prepared MMMs are examined. Surface morphology and distribution of carbon particles in mixed-matrix layer are tested by Scanning Electron Microscopy (SEM).

Outcomes

Influence of solvent-saturation process on pore blockage was investigated using EDX. Silicon ratio (Si) from the surface thorough the center of the carbon particles was evaluated at predefined depths (Figure 1). With and without saturation process, it has been detected that Si presence decreased inwards the particles. More polymer chains entrance into the filler particles was observed in the unsaturated carbon particles. Deeper PDMS penetration (up to 70 µm) has been detected in the unsaturated particles than saturated particles (up to 50 µm). Results proved that it is possible to reduce pore blockage with saturation process. As a further step, saturation experiments were repeated with different solvents and carbon particles, and degree of pore blockage is compared. As a result, achieving this goal makes MMMs more powerful and promising in gas separation processes.

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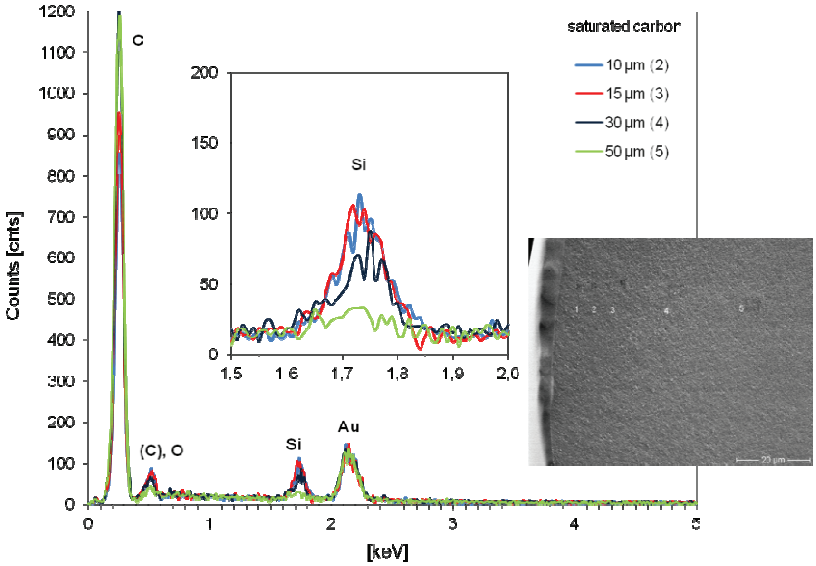

Figure 1. SEM picture and EDX-Analysis of a saturated carbon sample

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