Hybrid inorganic-organic membranes in the service of clean coal technologies

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Abstract Clean coal technologies (CCT) are all technological solutions that are designed to increase the efficiency of coal combustion, processing and extraction. They are therefore, all the technologies that will help to reduce its environmental nuisance during the production and use of coal and can be introduced at various stages of coal application. Earlier was stated that none of the energy sources (natural gas, crude oil and renewable energy sources), their native resources, the used technologies and the sources of imports are not able to eliminate hard coal from the energy mix of Poland in the near future. That is why the authors began research to create a new clean-coal technology based on the hybrid inorganic-organic membranes, which can be used for elimination of harmful substances generated during coal combustion, especially CO₂. This work concerns the study of the inorganic-organic hybrid membranes based on few modified polymer matrices and various inorganic fillers. It was found that incorporation of zeolite 4A into the polymer matrix had significantly changed the gas transport parameters (D, P, S and α). In turn, the mechanical (Rm and E) parameters have increased with the filler content. The application allows the initial selection of ingredients from which the final membrane will be created. The designed technology does not require high financial expenditures, and it is also highly universal. It can be used both in households, heating plants and, above all, in power plants.

1. Introduction

The term Clean Coal Technologies (CCT) refers to all technologies designed to increase both the efficiency and environmental acceptability of coal mining, preparation and use. They are therefore, all the technologies that will help to reduce its environmental nuisance during the production and use of coal and can be introduced at various stages of coal application. When coal is burned, various pollutants such as carbon dioxide (CO₂), sulfur dioxide (SO₂), nitrogen oxides (NOₓ), mercury and other chemical by-products are emitted into the atmosphere, that vary depending on the type of coal used. These emissions have a negative impact on the environment and human health, contributing to acid rain, lung cancer and cardiovascular disease. In order to reduce this negative impact, clean coal technologies (CCT) are introduced, which include chemical leaching of minerals and impurities from coal, its gasification, coal dewatering to improve the calorific value, flue gas cleaning technology, carbon dioxide capture and storage, etc. As there are still a number of problems with the cost-effectiveness of these technologies and the timing of their delivery, work continues to find the most optimal one [1, 2].
Nowadays, the main problems with the anthropogenic climate change and global warming are caused due to a drastic increase of atmospheric level of various greenhouse gases, like, for instance, CO$_2$ [3]. Over the last century, the rising CO$_2$ concentration in the atmosphere was caused by increasing activity within transportation, energy supply from fossil fuels [4, 5] and production of raw materials (steel, cement, etc.) [3]. The main strategy of reducing CO$_2$ emission is carbon capture and sequestration (CCS) including post-combustion, oxyfuel and pre-combustion processes [4, 6]. CO$_2$ separation is also very significant in other applications, like biogas production and natural gas sweetening [5, 8-11]. Such separated CO$_2$ can then be used in enhanced oil recovery (EOR) operations or to feed algae, phytoplankton or bacteria that enable the production of food, nutritional supplements, feed for livestock, methane and lipids, which can be converted into biofuel and even the algal plastic called polyethylene furandicarboxylate (PEF) [9]. So, it can be clearly seen that development of the appropriate CO$_2$ separation technologies is very important. However, conventional techniques are very energy-consuming, therefore their use is limited from environmental and economic reasons. The promising alternatives are membrane technologies since they are characterized by numerous advantages such as: low energy requirement, high efficiency, simple design, easiness of scale-up, economic and environmental kindliness [7, 12, 13]. Both inorganic and organic membranes are promising for CO$_2$ separation. However, each of both membrane types are characterized by advantages and disadvantages. The perfect solution to overcome their disadvantages – realizing indeed the trade-off between permeability and selectivity – would be the combination of their decent parameters in the form of hybrid inorganic-organic membranes [14, 15]. This type of membranes could be obtained via incorporation of inorganic materials (like, silica, metal oxides, CNTs, graphene, nanofibers, zeolites, CMS, MOFs, POFs, etc.) into the polymer matrix (like, PTMSP, PEBAX, Matrimid, PDMS, PVAc, PSF, CA, PPO, BSPPO, SPEEK, Ultrason, PIM-1, PIs, FPI, etc.) [3, 4, 6, 7, 8, 10, 12, 13, 16]. This usually leads to the creation of hybrid materials with enhanced gas transport, mechanical, thermal, electric or magnetic properties, adjusted by control of the composition, content and morphology of the filler addition, application of different processing techniques or by applied modification of both phases [14, 15]. These new hybrid materials with tailored properties have found the application in many areas. However, many problems, especially related to the production of hybrid membranes and ensuring appropriate properties, need to be solved. [17]. This is the key reason why the researchers are still looking for solutions to improve their processability, gas permeability and selectivity and membrane durability [18].

As part of research on the use of membrane techniques at Clean Coal Technologies, the authors synthesized various types of hybrid membranes based on various polymer matrices and inorganic additives, such as Fe@MWCNTs and zeolite 4A. This paper discusses CCT using the example of CO$_2$ selective hybrid inorganic-organic membranes zeolite 4A/SPEEK. The experimental results are compared with theoretical MOT 2.0-predicted data based on three leading models: Maxwell, Bruggeman and Lewis-Nielsen. MOT 2.0 (membrane optimisation tool) is a modern computer application for modelling of gas transport processes through hybrid inorganic-organic membranes [19].

2. Materials and Methods

2.1. Computer program MOT 2.0
In this paper, the experimental results were compared with the results predicted using the appropriate theoretical model which is an integral part of the modern computer application MOT 2.0 [19]. The MOT 2.0 (Membrane Optimization Tool) could be used for modelling of gas transport processes through hybrid membranes. The current version of the application is based on few models like, the Maxwell, Bruggeman and the next-generation Lewis–Nielsen model (Figure 1), allowing for the description of transport in more complex systems with the possibility of considering possible defects. This last model is given by the following formula [20]:
\[ p_r = \frac{P}{P_m} = \left[ 1 + 2\left(\frac{(\lambda_{dm} - 1)}{(\lambda_{dm} + 2)}\right)\Phi \right] \left[ 1 - \left(\frac{(\lambda_{dm} - 1)}{(\lambda_{dm} + 2)}\right)\Phi \psi \right] \]

where:

\[ \psi = 1 + \left(\frac{1 - \Phi_m}{\Phi_m^2}\right) \Phi \]

Pr - relative permeability of gas components; P - effective permeability of gas components in MMM; Pm - permeability of gas components in a polymer matrix (continuous phase); \( \Phi \) - volume fraction of filler particles; \( \lambda_{dm} \) - \( P_d/P_m \) permeability ratio; \( P_d \) - permeability of components in the dispersed phase; \( \Phi_m \) – the maximum packing volume fraction of filler particles (0.64 for random close packing of uniform spheres).

It was originally developed for elastic modulus of particulate composites, it covers a broad range of \( \Phi \) (0 < \( \Phi \) < \( \Phi_m \)) and is straightforward to solve for permeability. Furthermore, it takes into an account the effects of morphology (a particle shape, the particle size distribution and aggregation of particles) on permeability through the parameter \( \Phi_m \).

**Figure 1. Lewis-Nielsen model window**

The elaborated and developed application MOT 2.0 allows for optimisation of membrane parameters in the stage of its design – such as permeability and selectivity. It also has additional options such as: the possibility of entering empirical data \((P, \alpha)\) to present them on the graph together...
with theoretical data and comparison with Robeson upper bound line, calculation of sorption and diffusion coefficients, calculation of model error (AARE) as well as optimisation of the $\Phi$ value relatively to the desired value of $P$ and $\alpha$.

2.2. Membrane preparation and characterization
The homogeneous and inorganic-organic hybrid membranes based on SPEEK matrix and various additions of primed zeolite 4A as fillers (zeolite 4A: 10-40% wt%) were examined. The zeolite 4A/SPEEK membranes were obtained from the dispersion of primed zeolite (particles pre-coated with a thin layer of polymer) in a 9% SPEEK solution in DMAc, obtained by sonication for 3 h. The suspensions thus prepared were poured into levelled Petri dishes and heated at 60 °C for 12 h, and then at 80 °C for the next 12 h. Gas ($\text{CO}_2$ and $\text{N}_2$) permeability measurements were conducted for membranes on the low-pressure gas permeation analyzer IDP-2 [21-26]. Measurements were carried out at temperature of 25 °C. These flow-rate data were used to evaluate the mass transport coefficients ($D$, $P$, $S$ and $\Phi$), using the Time Lag method.

3. Results and discussions
The main permeation data for zeolite 4A/SPEEK hybrid membranes were shown in Figure 2 and 3.

![Figure 2. Dependence of the gas transport coefficients versus zeolite 4A concentration in the SPEEK hybrid membranes](image-url)
Figure 3. Dependence of a selectivity coefficient $\alpha_{CO_2/N_2}$ versus: a) filler concentration in the various hybrid membranes and b) permeation coefficient $P$ regarding the Robeson upper bound line

Incorporation of zeolite 4A into the polymer matrices has significantly altered their gas transport properties. It was observed that with the increasing filler addition, the zeolite 4A/SPEEK hybrid membranes were characterized by the rise of both the CO$_2$ permeability and selectivity. It was found that the measurements points approaching Robeson’s upper bound line (Fig.3b) along with the increase in filler content. So, it can be seen that after modification of both the zeolite 4A and polymer matrix, it was possible to obtain more productive membrane. The used Lewis–Nielsen model proved to be suitable for describing the CO$_2$ transport through the analyzed membranes, the %AARE error was only 10%. Such a good correlation can be associated with taking into account the effects of morphology (a particle shape, the particle size distribution and aggregation of particles) on permeability through the parameter $\Phi_m$. Sulfonation of the PEEK matrix and its interaction with OH groups on the zeolite surface (hydrogen bonds) allowed to increase the compatibility of the organic and inorganic phase, thus increasing the permeability and selectivity of the obtained hybrid membranes. These modifications also limited the number of voids and possible defects. Also the mechanical ($R_m$ and $E$) parameters of these membranes have increased with the filler content.

4. Conclusions
Inorganic-organic hybrid membranes based on SPEEK and zeolite 4A as filler were successfully synthesized and characterized. It was found that incorporation of fillers into polymer matrix had significantly improved gas transport and mechanical parameters of analysed membranes. The used Lewis–Nielsen model proved to be suitable for describing the CO$_2$ transport through hybrid membranes. These membranes seem to be appropriate for CO$_2$ separation from flue gases, especially after the introduction of chemical modifications (increase of inter-phase compatibility and the affinity to CO$_2$). The proposed membrane technology based on CO$_2$ selective SPEEK/zeolite 4A hybrid membranes perfectly fits into Clean Coal Technologies. It may, in the future, be a solution to the problems associated with cleaning flue gases from greenhouse gases.

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