Hybrid inorganic-organic membranes based on iron-encapsulated carbon nanotubes and their application in CO_2 separation

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Introduction

Nowadays, considering the problems with climate change and global warming caused by the increase in greenhouse gas emissions, mainly CO_2, (mainly from energy production and transport), there was a need to reduce it. CO_2 separation can be carried out by various conventional methods, however most of them are very energy-consuming and expensive. A real alternative to them can be membrane techniques, based on the latest type of hybrid membranes, combining the advantages of both organic and inorganic membranes. This work concerns the study of the inorganic-organic hybrid membranes based on FeSPEEK polymer matrix and various additions of Fe@MWCNT-OH as a filler.

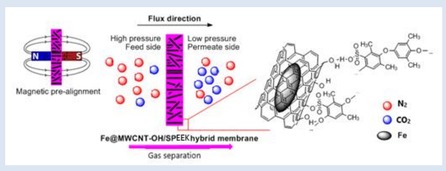
Synthesis and modification of Fe@MWCNTs

Fe@MWCNTs were synthesized via catalytic Chemical Vapor Deposition (c-CVD) at 760°C in an argon flow using toluene and ferrocene (5.6 wt.%) as main carbon and catalyst precursor, respectively. The average outer and inner diameters were 60±25 and 10±2 nm, respectively. The Fe@MWCNTs were then hydroxylated using an aqueous solution of hydrogen peroxide (30 wt%).

Membrane preparation and characterization

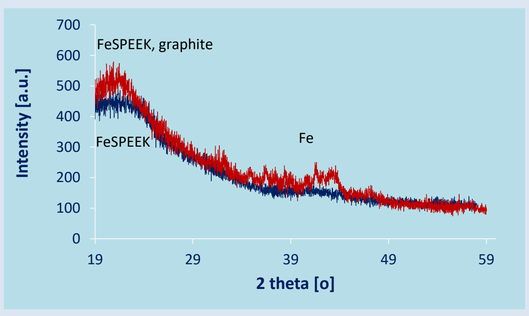
The homogeneous and inorganic-organic hybrid membranes based on a FeSPEEK matrix and various additions of Fe@MWCNT-OH as filler (CNTs: 0.5-10.0 wt%) were examined. These membranes were made by casting of filler particles sonicated dispersions in polymer solutions without or within a magnetic field (B=40 mT or B=100 mT). Gas (CO_2 and N_2) permeability measurements were conducted for membranes on the low-pressure gas permeation analyzer IDP-2. Measurements were carried out at temperature of 25°C. These flow-rate data and percentage of the air enrichment were used to evaluate the mass transport coefficients (D, P, S and a), using Time Lag method. The magnetic properties of membranes were examined by means of a Lake Shore 7010 vibrating sample magnetometer (VSM) and mechanical properties using static testing machine Zwick/Roell Z050. TGA analysis was also performed using a Linseis STA PT1600 thermobalance (Selb, Germany). The prepared membranes were also characterized using XRD (Rigaku Mini-Flex II diffractometer with Cu Kα radiation).

Scheme of hybrid membrane preparation and gas permeation process



Experimental setup IDP-2

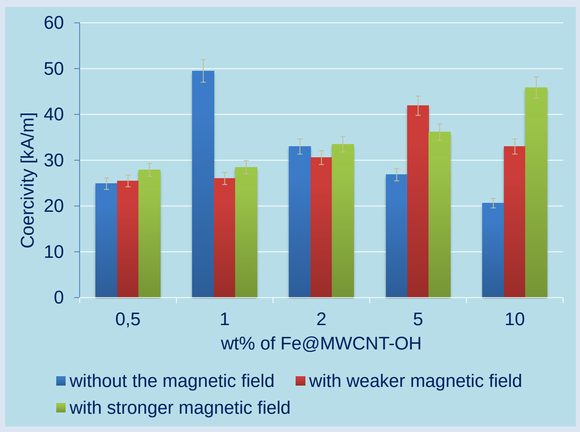
XRD spectrum for Fe@MWCNT-OH/FeSPEEK hybrid membrane

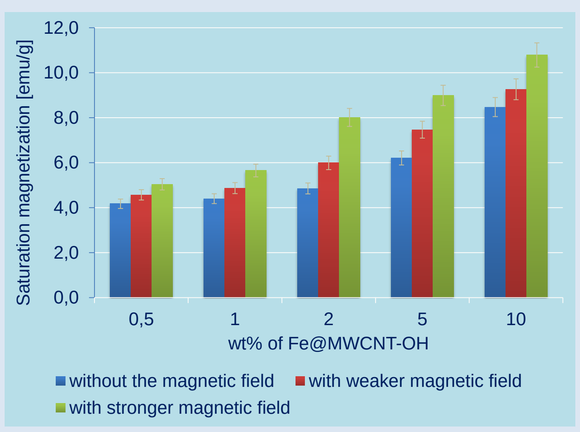


XRD analysis shown the presence of peak characteristic for the polymer matrix FeSPEEK (21,5°C) and for Fe@MWCNT's (42,9° and 44,7° for α-Fe and γ-Fe, and 25,8°, 42,3° for graphite).

Magnetic properties

Dependence of hybrid membrane's coercivity and saturation magnetization on Fe@MWCNT-OH loading



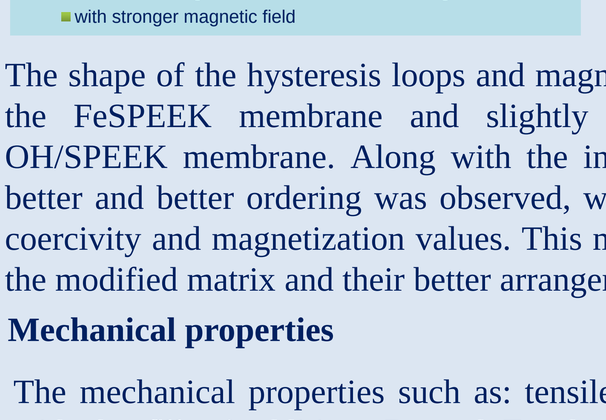


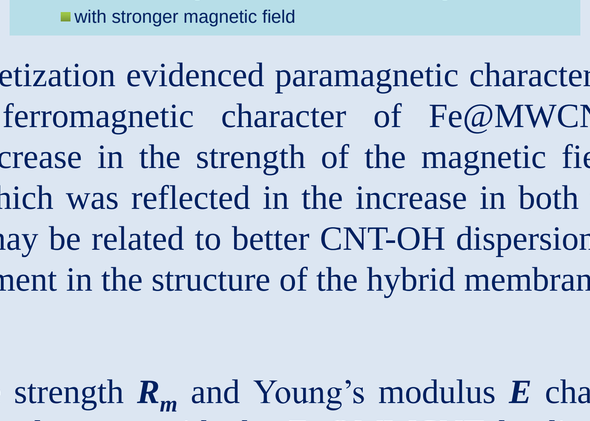
The shape of the hysteresis loops and magnetization evidenced paramagnetic character of the FeSPEEK membrane and slightly ferromagnetic character of Fe@MWCNT-OH/SPEEK membrane. Along with the increase in the strength of the magnetic field, better and better ordering was observed, which was reflected in the increase in both the coercivity and magnetization values. This may be related to better CNT-OH dispersion in the modified matrix and their better arrangement in the structure of the hybrid membrane.

Mechanical properties

The mechanical properties such as: tensile strength $\boldsymbol{R_m}$ and Young's modulus $\boldsymbol{E}$ change with the fillers' addition. $\boldsymbol{R_m}$ and $\boldsymbol{E}$ values decrease with the Fe@MWCNT loading in membranes cast without a magnetic field. While the $\boldsymbol{R_m}$ and $\boldsymbol{E}$ values increased with the filler loading in magnetic-cast membranes, especially in a stronger magnetic field. This improvement is caused by the reduction of overall polymer chains mobility, increase of density of hybrid membranes and CNT's appropriate alignment in membrane's structure. Enhancement of the mechanical properties translates directly into better separation properties of hybrid membranes and their potential use in the future.

The dependency of *Rm* and *E* vs. Fe@MWCNT-OH loadings for FeSPEEK membranes cast in various magnetic conditions



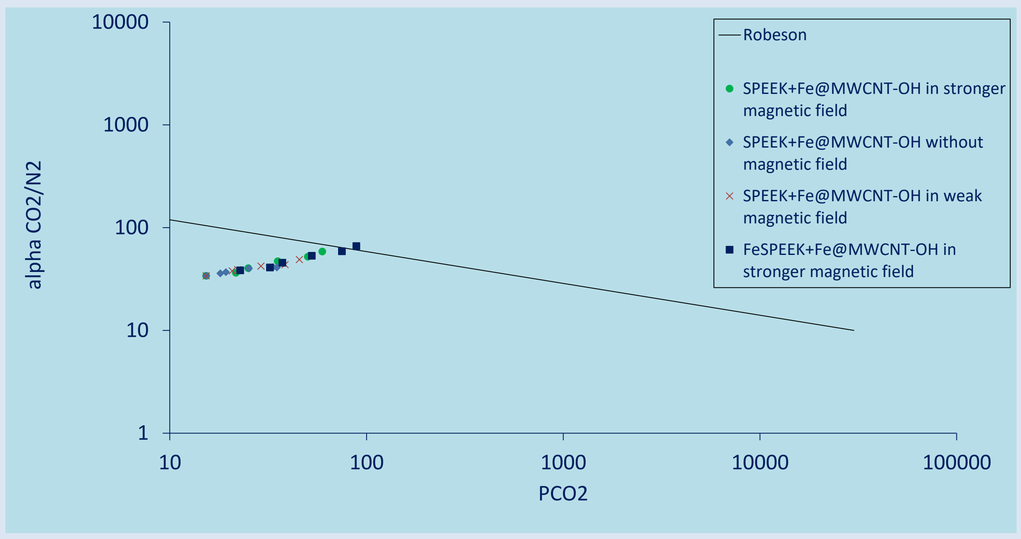


Gas permeation results

Dependence of the gas transport coefficients vs. Fe@MWCNT-OH loading in FeSPEEK hybrid membranes prepared without a magnetic field

Dependence of the gas transport coefficients vs. Fe@MWCNT-OH loading in FeSPEEK hybrid membranes prepared in a stronger magnetic field

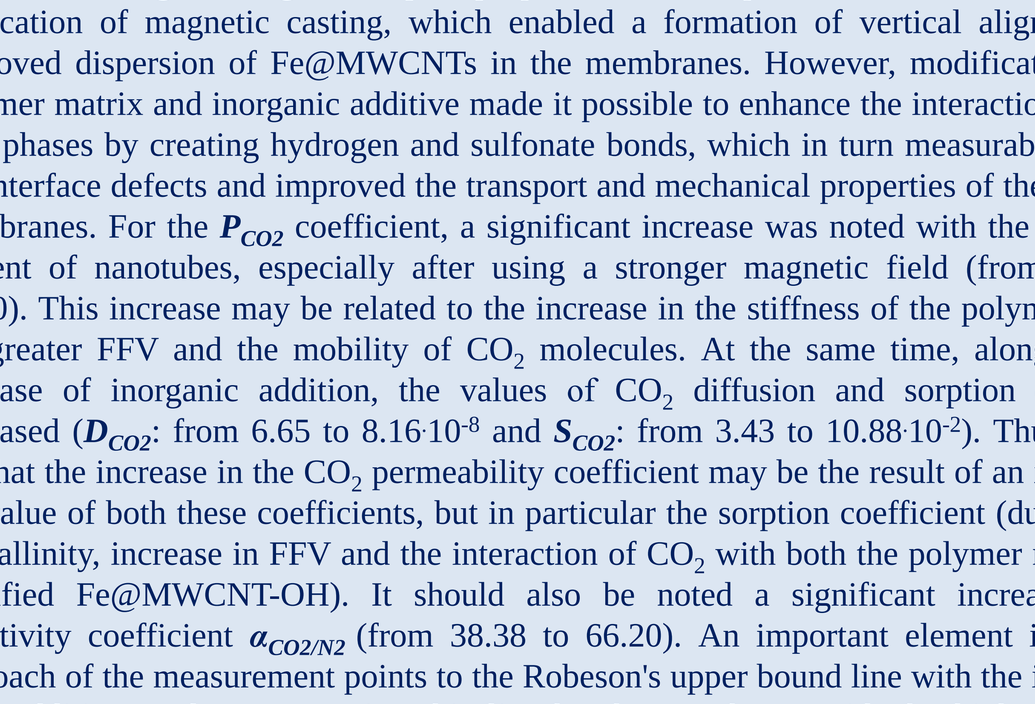
Dependence of the selectivity coefficient $\alpha_{CO2/N2}$ versus permeation coefficient P_{CO2} regarding the Robeson upper bound line



The incorporation of Fe@MWCNT-OH into the modified polymer matrix had significantly changed the transport parameters (D, P, S and α) of gases transported through those hybrid membranes. In general, gas transport properties were improved, to a certain extent, by application of magnetic casting, which enabled a formation of vertical alignment and improved dispersion of Fe@MWCNTs in the membranes. However, modification of the polymer matrix and inorganic additive made it possible to enhance the interaction between both phases by creating hydrogen and sulfonate bonds, which in turn measurably reduced the interface defects and improved the transport and mechanical properties of the produced membranes. For the $\boldsymbol{P_{CO2}}$ coefficient, a significant increase was noted with the increasing content of nanotubes, especially after using a stronger magnetic field (from 22.80 to 88.80). This increase may be related to the increase in the stiffness of the polymer chains, the greater FFV and the mobility of CO_2 molecules. At the same time, along with the increase of inorganic addition, the values of CO_2 diffusion and sorption coefficient increased ($\boldsymbol{D_{CO2}}$: from 6.65 to $8.16 \cdot 10^{-8}$ and $\boldsymbol{S_{CO2}}$: from 3.43 to $10.88 \cdot 10^{-2}$). Thus, we can see that the increase in the CO_2 permeability coefficient may be the result of an increase in the value of both these coefficients, but in particular the sorption coefficient (due to lower crystallinity, increase in FFV and the interaction of CO_2 with both the polymer matrix and modified Fe@MWCNT-OH). It should also be noted a significant increase in the selectivity coefficient $\boldsymbol{\alpha_{CO2/N2}}$ (from 38.38 to 66.20). An important element is also the approach of the measurement points to the Robeson's upper bound line with the increase of filler addition, and even crossing this line by the membrane with the highest 10 wt% addition of Fe@MWCNT-OH.

Thermal analysis of Fe@MWCNT-OH/FeSPEEK membranes

TGA results for Fe@MWCNT-OH/FeSPEEK hybrid membranes with various Fe@MWCNT-OH addition



It should be noted that with the increase of Fe@MWCNT-OH addition, the maximum of the peaks responsible for the subsequent transformations are shifted towards higher temperatures. This may indicate better thermo-oxidative properties of the obtained hybrid membranes.

Conclusions

It was found, that:

- magnetic and mechanical parameters $\boldsymbol{R_m}$ and $\boldsymbol{E}$ increased with the Fe@MWCNT-OH loading in membranes cast in a magnetic field, especially a stronger one
- incorporation of Fe@MWCNT-OH into the polymer matrix can alter their gas transport properties
- gas transport properties (D, P, S and α) were improved by application of magnetic casting, which enabled a formation of vertical alignment and improved dispersion of Fe@MWCNT-OH in the membranes
- application of the modified FeSPEEK polymer matrix allowed to obtain better adhesion between inorganic and polymer phase, which resulted in the increase of CO_2 permeability and selectivity
- the obtained hybrid membranes are characterized by better thermo-oxidative properties