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Proceeding Paper

Hybrid Inorganic-Organic Membranes Based on Iron-Encapsulated Carbon Nanotubes and Their Application in CO_2 Separation †

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Abstract: The article proposes the use of hybrid membranes based on a FeSPEEK matrix and an inorganic addition in the form of modified Fe@MWCNT-OH nanotubes for CO_2 separation. It was found that the introduction of nanofillers to the polymer matrix resulted in a significant improvement in CO_2 permeability and selectivity of membranes. The use of magnetic casting of membranes improved the alignment and dispersion of Fe@MWCNT-OH carbon nanotubes in the polymer matrix. On the other hand, additional chemical modification of the polymer matrix and nanotubes allowed to increase the interfacial compatibility and the efficiency of hybrid membranes. The increase in the inorganic additive had a positive effect on both the thermo-oxidative stability as well as the mechanical and magnetic parameters of the hybrid membranes.

Keywords: Fe@MWCNT-OH; CO_2 separation; inorganic-organic hybrid materials; mechanical properties; magnetic properties; thermal parameters

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1. Introduction

Nowadays, there is a need to reduce greenhouse gas emissions, especially CO_2, due to accelerating climate change and global warming. As conventional CO_2 separation methods are generally costly and energy-consuming, alternative methods are being sought. They can become membrane technologies based on properly constructed membranes, characterized by increased permeability and selectivity, good mechanical strength, and chemically and thermally stable [1,2]. Both organic and inorganic membranes can be used, but in addition to numerous advantages, they also have disadvantages. Therefore, a promising solution may be inorganic-organic hybrid membranes, combining the advantages of both types of membranes [3]. They can be obtained by introducing inorganic additives into the polymer matrix [4,5]. The basic problem in their synthesis is the appropriate compatibility between the organic and inorganic phases, which is directly related to the selection of an appropriate polymer matrix and inorganic additive. This article proposes the application of a modified FeSPEEK polymer matrix and the Fe@MWCNT-OH inorganic additives to create membranes used in CO_2 separation. The obtained hybrid membranes were also tested using static mechanical performance, thermogravimetry (TGA), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM).

2. Methods

2.1. Fe@MWCNT-OH/FeSPEEK Membrane Preparation and Characterization

As part of the article, both homogeneous and heterogeneous membranes, based on a modified FeSPEEK polymer matrix and various additives of Fe@MWCNT-OH nanotubes, were investigated. The first step in their preparation was the synthesis of Fe@MWCNTs by catalytic Chemical Vapor Deposition (c-CVD) using toluene and ferrocene (760 °C in an argon flow). The obtained nanotubes were further hydroxylated with the aqueous solution of hydrogen peroxide (30 wt%). Then suspensions of Fe@MWCNT-OH in a 9% NaSPEEK solution in DMAc were prepared, which, after 3 h of sonication, were poured onto leveled Petri dishes placed in an external magnetic field (Figure 1., B = 40 mT or B = 100 mT) and the solvent was evaporated gradually increasing the temperature (60 °C for 12 h, and next 80 °C for 12 h). After 2 days of soaking in iron dichloride aqueous solutions (nitrogen atmosphere), Fe@MWCNT-OH/FeSPEEK membranes were obtained. For the membranes obtained in this way, a CO_2 and N_2 permeation study was carried out using the low-pressure gas permeation analyzer IDP-2, described elsewhere [6,7] at the temperature of 25 °C. Based on the obtained data, mass transport coefficients, such as D, P, S, and α, were determined [8,9].

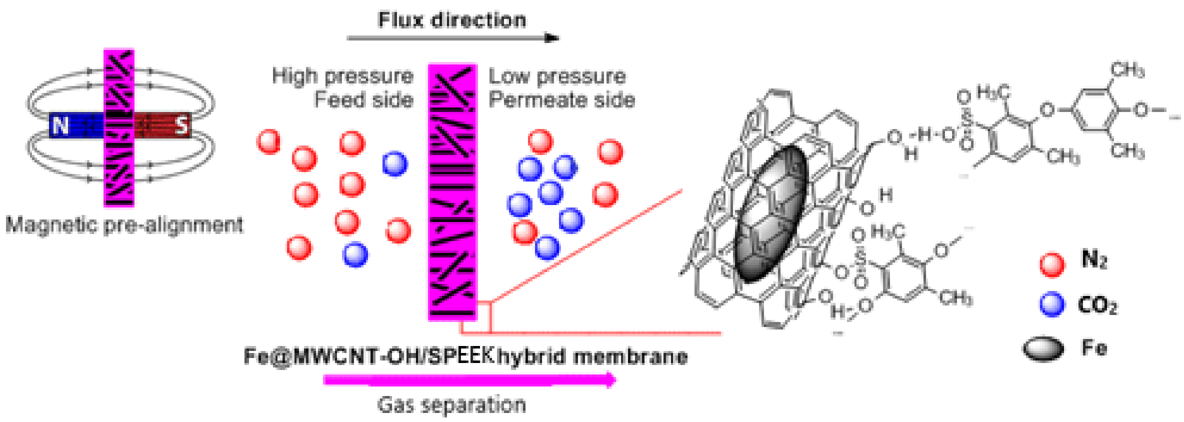


Figure 1. Scheme of Fe@MWCNT-OH/FeSPEEK membrane preparation and their application in gas separation.

The Zwick/Roell Z050 static testing machine was used to test the mechanical properties of membranes. On the other hand, the Lake Shore 7010 vibration magnetometer (VSM) was used to analyze their magnetic parameters. Thermal properties were investigated using a Linseis STA PT1600 thermobalance (Selb, Germany). The membranes were also characterized using Rigaku Mini-Flex II diffractometer (with Cu Kα radiation).

3. Results and Discussion

3.1. Mechanical and Magnetic Properties of Fe@MWCNT-OH/FeSPEEK Membranes

Based on the analysis of the mechanical properties, it was found that values of tensile strength $\boldsymbol{R_m}$ and Young's modulus $\boldsymbol{E}$ decrease with the Fe@MWCNT-OH addition in membranes cast without a magnetic field. While the $\boldsymbol{R_m}$ and $\boldsymbol{E}$ values increased with the filler addition in magnetic-cast membranes, especially in a stronger magnetic field (Figure 2). This improvement is caused by the increase of membrane's density, reduction of polymer chains mobility, and CNT's appropriate alignment in membrane's structure.

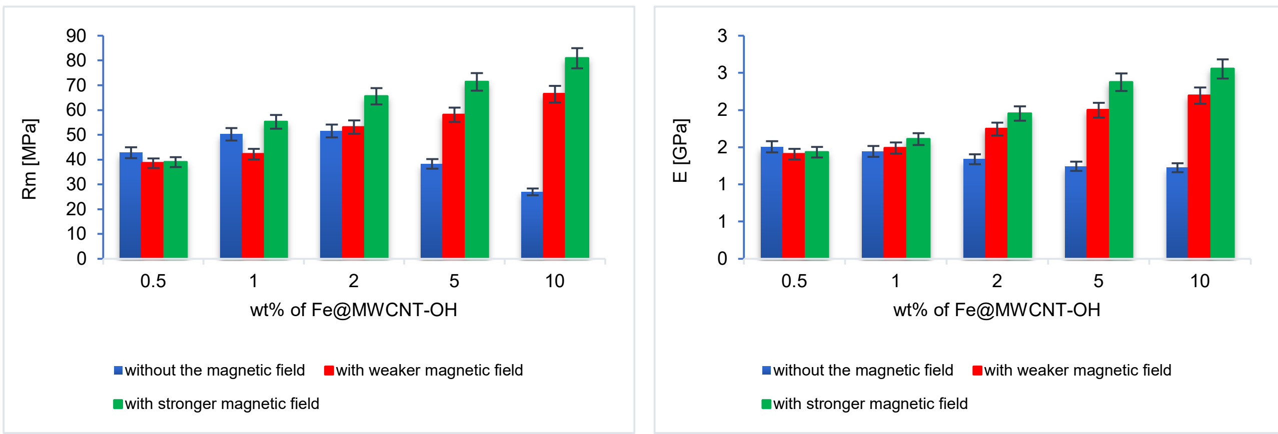


Figure 2. Dependence of (**a**) tensile strength R_m and (**b**) Young's modulus E vs. Fe@MWCNT-OH loadings for hybrid membranes cast under various magnetic conditions.

XRD analysis (Figure 3) shown the presence of peaks characteristic for the polymer matrix FeSPEEK (21.6 °C) and for Fe@MWCNT's (42.9° and 44.7° for α-Fe and γ-Fe, and 25.8°, 42.3° for graphite). Considering the influence of the magnetic field on the membrane production process and their subsequent properties, the magnetic parameters of the hybrid membranes were investigated (Figure 2).

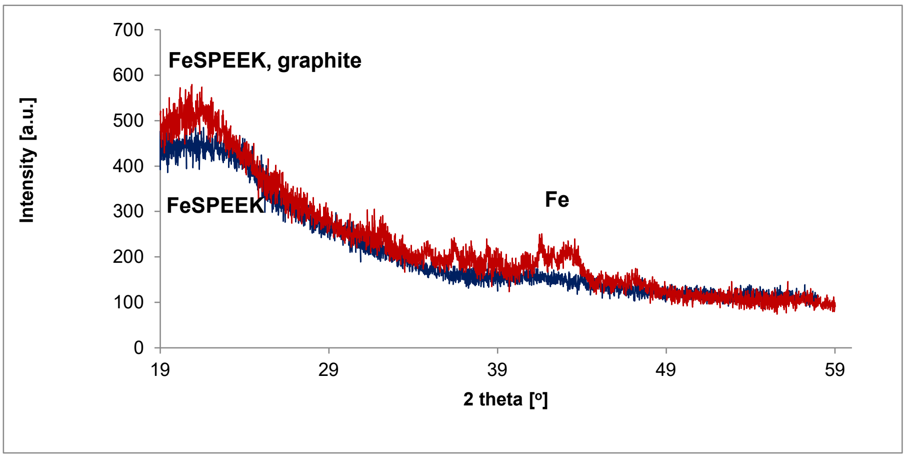


Figure 3. X-ray diffraction spectra for hybrid Fe@MWCNT-OH/FeSPEEK and homogeneous FeSPEEK membrane (1 wt%).

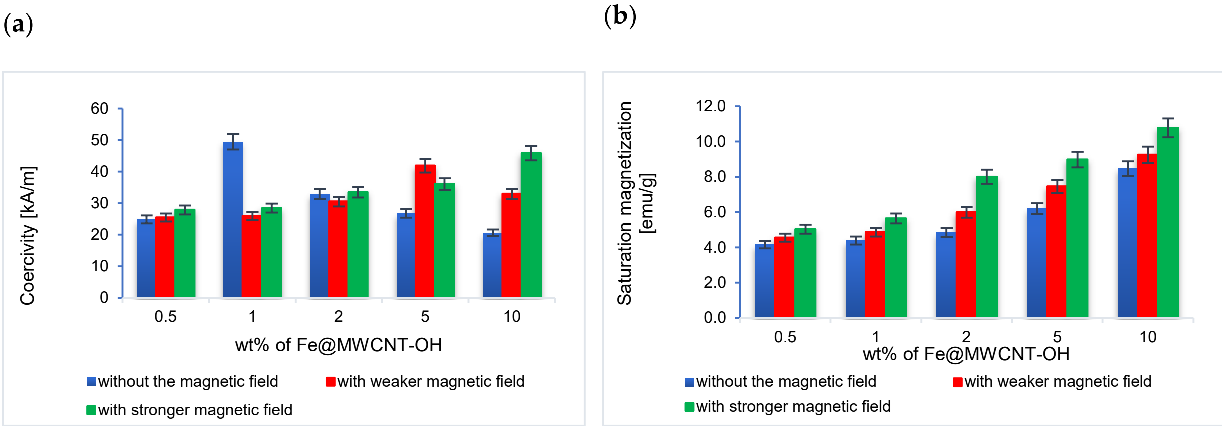


Figure 4. Dependence of (**a**) coercivity and (**b**) saturation magnetization vs. Fe@MWCNT-OH loading for hybrid membranes cast under various magnetic conditions.

Based on the shape of the hysteresis loops and the values of magnetization, the paramagnetic nature of the FeSPEEK homogeneous membrane and the slightly ferromagnetic nature of the Fe@MWCNT-OH/SPEEK hybrid membrane were found. 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 Fe@MWCNT-OH dispersion in the modified matrix and their better arrangement in the structure of the hybrid membrane.

3.2. Thermal Analysis of Fe@MWCNT-OH/FeSPEEK Membranes

TGA was performed to study the thermal properties of hybrid membranes as shown in Figure 5.

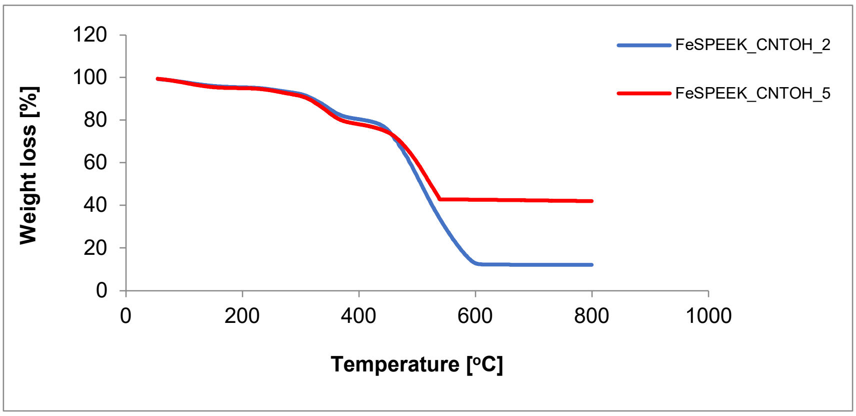


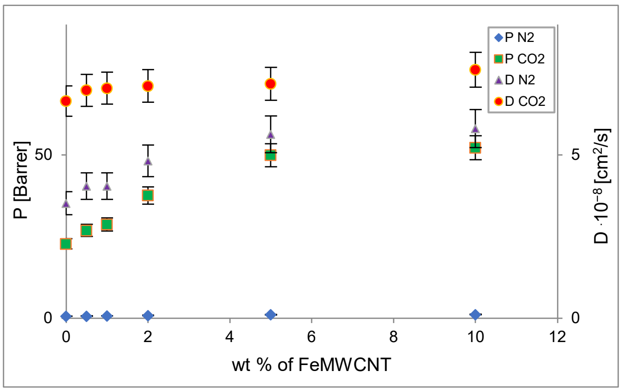
Figure 5. TGA curves obtained for Fe@MWCNT-OH/FeSPEEK membranes with various Fe@MWCNT-OH loading.

Based on the obtained results, it was found that the maxima of the peaks characteristic for successive transformations shift towards higher temperatures with the increase of Fe@MWCNT-OH addition and the membranes do not degrade below 225 °C (Figure 5). Registered weight losses for hybrid membranes are significantly lower than for homogeneous membranes, and they also decrease with increasing Fe@MWCNT-OH loading. Thus, it can be concluded that the addition of modified nanotubes has a positive effect on the thermo-oxidative properties of the obtained hybrid membranes.

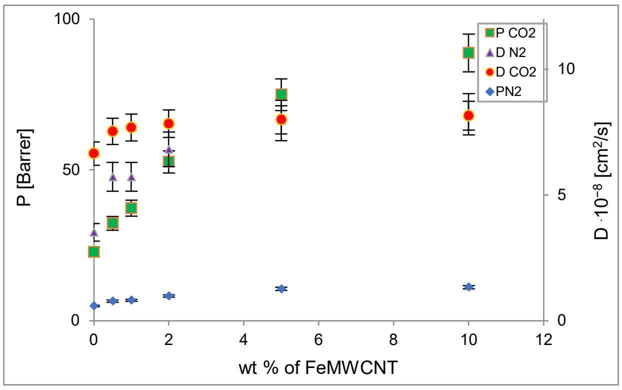
3.3. Gas Transport Properties of Fe@MWCNT-OH/FeSPEEK Hybrid Membranes

The synthesized hybrid membranes were examined for their potential use in CO_2 separation. Figure 6 shows the parameters of CO_2 and N_2 transport through the tested Fe@MWCNT-OH/FeSPEEK membranes.

(**a**)



(**b**)



(**c**)

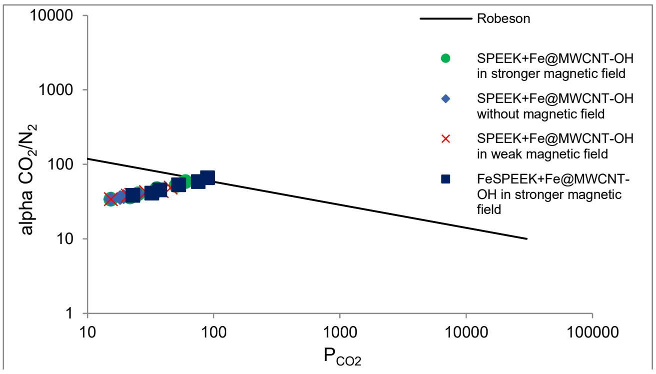


Figure 6. Dependence of (**a**) diffusion and permeation coefficients vs. Fe@MWCNT-OH addition in the hybrid membranes cast in the magnetic field with an induction of 0 mT, (**b**) cast in the magnetic field with an induction of 100 mT and (**c**) selectivity coefficient $\alpha_{CO2/N2}$ vs. permeation coefficient P_{CO2}.

It was found that the introduction of Fe@MWCNT-OH into the modified polymer matrix positively influenced the gas transport parameters (D, P, S and α). The use of the magnetic field during the production of hybrid membranes allowed for the proper ordering of the inorganic additive and improved its dispersion in the polymer matrix.

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. It was noted that permeability of CO_2 through dense membrane due to the substitution by Fe^{2+} ions was lower, while the selectivity increased. It was probably caused by the increased density of polymer matrix and its crosslinking, free volume decrease, increased polarity, and interaction between polymer chains. However, with increasing Fe@MWCNT-OH addition (due to the interaction with FeSPEEK matrix), the CO_2 permeability and selectivity increase both. For the 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 (D_{CO2}: from 6.65 to

8.16×10^{-8} and S_{CO2}: from 3.43 to 10.88×10^{-2}). Thus, we can see that the increase of the CO_2 permeation coefficient may be the result of an increase in the value of both these coefficients, but in particular the sorption coefficient (increase of FFV, lower crystallinity, and the interaction of CO_2 with both the polymer matrix and modified Fe@MWCNT-OH). This is possibly related to the electrical nature of the CO_2 molecule. It has a quadrupole moment, which in turn leads to a much stronger interaction with the polar groups compared to the nitrogen molecule. It should also be noted a significant increase in the value of $\alpha_{CO2/N2}$ (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 rise of filler loading, and even crossing this line by the membrane with the highest 10 wt% addition of Fe@MWCNT-OH.

3. Conclusions

As part of the article, a new type of hybrid membranes was synthesized, based on FeSPEEK as a polymer matrix and Fe@MWCNT-OH as a filler. It was noted that the use of iron-encapsulated carbon nanotubes as nanofillers, chemical modification of both phases and the application of the magnetic field during the production of membranes positively influenced the CO_2 transport properties (D, P, S and $\alpha_{CO2/N2}$). The magnetic, mechanical, and thermal properties have also improved significantly. Therefore, the proposed solution in the form of CO_2 selective Fe@MWCNT-OH/FeSPEEK membranes could be used in the power industry in the future.

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