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Fabrication and Characterization of MOF-Doped Composite Polyvinyl Alcohol Membrane and Investigation of Its Potential for Carbon Dioxide Separation from Flue Gas

Filiz Uğur Nigiz[1]

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Abstract − The objective of this work was to prepare glassy polymeric membranes to separate carbon dioxide from flue gas mixtures and conduct gas separation experiments using these membranes. Metal-organic framework (MOF) was added to the membranes to improve their ability to select carbon dioxide, thereby enhancing the strength of the membrane and gas separation performance. Therefore, MIL 140B was synthesized, and composite polyvinyl alcohol membranes were prepared, characterized, and tested for carbon dioxide nitrogen removal. Increasing MIL 140B content significantly increased the tensile strength and mechanical strength. However, a significant decrease in mechanical strength was observed at 4 wt.% of the filler-doped membrane. In gas separation studies, first, single gas and then mixed gas tests were performed. In both cases, the MIL 140B additive increased both carbon dioxide selectivity and permeability. MIL 140B ratio increased from 0 wt.% to 4 wt.%, CO_2 permeability increased from 92 Barrer to 179 Barrer, and selectivity increased from 41.4 to 58.7.

Keywords − *Composite membrane, gas separation, metal-organic frameworks, polyvinyl alcohol*

1. Introduction

Carbon dioxide (CO_2) is essential for all life on Earth. It serves as the primary carbon source for biological processes in the atmosphere. Plants and algae utilize photosynthesis to transform CO_2 into carbohydrates, while aerobic organisms generate CO_2 as a byproduct of metabolic processes. The escalating presence of anthropogenic carbon dioxide in the atmosphere poses a burgeoning issue that can potentially have far-reaching ramifications for life on our planet. The increase in atmospheric CO_2 is mostly attributed to the emission of CO_2 resulting from the combustion of fossil fuels. Since CO_2 is a greenhouse gas, it absorbs infrared radiation, then more energy is released into the atmosphere. Therefore, it causes a temperature rise. Reducing dependence on fossil fuels through increased use of "green" energy (wind, solar, nuclear, etc.) lowers CO_2 emissions. If this cannot be avoided, the CO_2 created during combustion must be disposed of before it is discharged into the atmosphere. Methods for capturing and separating CO_2 are used to lower emissions from burning fossil fuels.

Gas separation technologies enable the separation of carbon dioxide from other gases. Separating a desired gas from any combination of gases is known as gas separation. When choosing the components of the gas mixture for gas separation, factors such as the process's cost, degree of purity, molecular structure, and physical

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[1] filiz.ugur@comu.edu.tr (Corresponding Author)
[1] Department of Chemical Engineering, Faculty of Engineering, Çanakkale Onsekiz Mart University, Çanakkale, Türkiye

characteristics are considered. Methods for separating gases come in four varieties. These include membrane-based gas separation, gas adsorption, gas absorption, and cryogenic distillation. Among these methods, membrane-based gas separation systems have several benefits, including easy scaling up, energy efficiency, and environmental safety.

A selective membrane is used to purify or separate gases in the physicochemical process of membrane gas separation. In particular, dense and non-porous membranes are utilized in membrane gas separation. Therefore, the solution diffusion model is frequently used to characterize membrane gas separation. This occurrence suggests that the effectiveness of the gas separation process is influenced by the soluble state of the gases in the structure of the membrane and the speed of passage through the membrane. The process is driven by the pressure gradient. Hence, operating parameters like pressure, gas content, and temperature greatly impact how well a separation goes.

The membrane's structural feature is the main aspect influencing the performance of gas separation, other than the operating conditions. It is possible to utilize inorganic, organic (polymeric), or composite membranes according to the needs of the process. Applications requiring high temperatures and chemicals are suitable for inorganic membranes [1-6]. Due to several advantages over inorganic membranes, including affordability, simplicity of modification, and ease of membrane synthesis, polymeric materials are frequently preferred [7, 8].

The effectiveness of the process is determined by the values of permeability and selectivity. The membrane's capacity for selective gas separation is represented by its selectivity, whilst its permeability describes its productivity. Diffusion selectivity and sorption selectivity are two crucial characteristics that influence the permeability/selectivity correlation [9]. Gas molecules transfer through the membrane's holes in the polymer matrix after being absorbed by the polymer [10]. The size of the penetrating molecules directly affects the diffusion selectivity. In comparison, gases with small molecules move more slowly than large ones [11]. The efficacy of gas separation is also influenced by sorption selectivity, which can result from strong or weak interactions between the polymer and the gas [12].

By enhancing the contact between the polymer and filler, mixed matrix polymeric membranes—also called composite membranes—are more effective at improving selectivity in gas separation processes [13, 14]. Two types of fillers are added to polymeric membranes: porous and non-porous fillers. Among the porous fillers, zeolite and metallic organic fillers enhance the polymeric matrix's gas separation capabilities [3, 15, 16].

An increase-decrease behavior between permeability and selectivity is frequently seen during gas separation when polymeric membranes are utilized without modification. Enabling modification procedures like mixing, crosslinking, or adding inorganic components may hinder the membrane's ability to separate gases. The permeability of membranes is significantly improved by the mixed matrix membrane manufacturing process, which incorporates micro/nanofillers into the polymeric matrix, as opposed to previous modification procedures [17, 18]. Fillers are added to polymeric membranes to enhance their functionality. Gas permeability values are raised by porous additives like zeolites and silicates, while non-porous materials are also utilized to enhance the target gas's selectivity.

The potential of metal-organic frameworks (MOFs) in adsorption and membrane separation processes has garnered significant interest. MOFs are able to provide a large deal of chemical and structural diversity because of their wide range of building blocks and modifiability [19, 20]. Hence, MOFs are more appealing as inorganic fillers in mixed-matrix membranes than traditional fillers (zeolites, silicas, or activated carbons) since they may be modified as needed for the selective adsorption of gases. More crucially, the organic component of MOFs makes a major improvement in the compatibility between filler and matrix achievable in MOF-based membranes. For effective CO_2 separation, MOF-doped composite membranes are crucial [21, 22].

This work aimed to prepare glassy polymeric membranes to separate carbon dioxide from flue gas mixtures and conduct gas separation experiments using these membranes. Metal-organic lattice (MOF) was added to the membranes to improve their ability to select carbon dioxide, thereby enhancing the strength of the membrane and gas separation performance.

2. Materials and Methods

2.1. Materials

Polyvinyl alcohol (PVA), zirconium chloride ($ZrCl_4$), and 2,6-naphthalenecarboxylic acid (H_2NDC) were supplied from Sigma Aldrich, Türkiye. Dimethylformamide (DMF) (99 % purity), acetic acid, and ethanol (99% purity) were purchased from Merck Chemical, Türkiye.

2.2. MOF Preparation

In the synthesis of MIL 140B, the procedure applied by [23] was modified and used. 0.688 grams of $ZrCl_4$ and 1.297 grams of H_2NDC were dissolved in 30 ml of dimethylformamide (DMF). The solution was taken into a Teflon container, placed in a hydrothermal reactor, and kept in a 220°C oven for six hours. The cooled MOF particles were washed with acetic acid and ethanol. Then, it was filtered and treated at 60°C for two hours.

2.3. Membrane Preparation

For polyvinyl alcohol (PVA) membrane, an aqueous solution containing 7 wt.% PVA is stirred at 80°C for 5 hours. Separately, 1-4 wt.% MIL 140B distributed in 5 mL of distilled water by using an ultrasonic homogenizer (Bandelin, Sonorex 4050) and added to the polymer solution. The solution was stirred at room temperature for two hours and degassed under vacuum. The solution was poured onto the glass surface and pulled with a film apparatus. The membranes, which had 60 µm thicknesses, were dried at room temperature for 1 day.

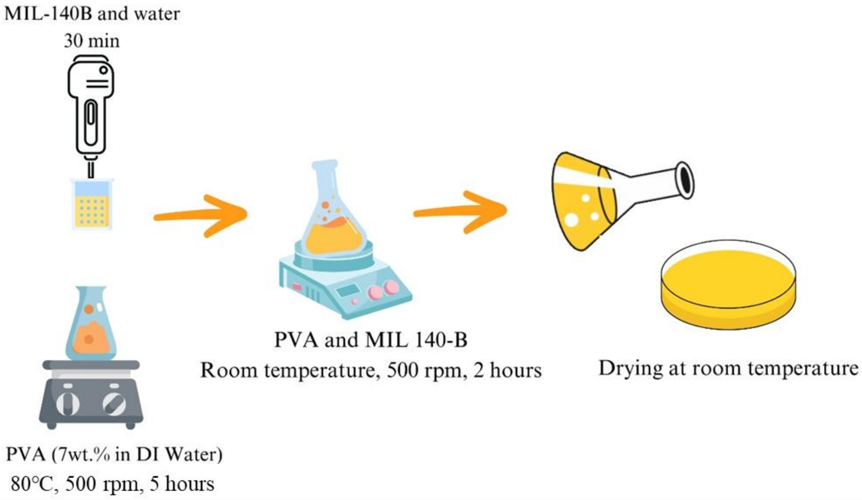

Figure 1. Schematic representation of nanocomposite membrane preparation

2.4. Gas Separation

The membrane permeability test system consists of a stainless-steel membrane cell (7 cm^2 area (A), 150 µm thickness (l) for casting film membrane, upper and lower pressure control parts, and a lower flow meter. The test was performed at room temperature with the upstream pressure of 2 atm. The prepared membranes were placed in the permeation system (Figure 2), and the individual permeabilities (P) of carbon dioxide and nitrogen were calculated from (2.1).

$$P = (\mathrm{Q.l})/\mathrm{A}.\Delta P \tag{2.1}$$

Then, carbon dioxide/nitrogen ideal selectivities (α) were calculated depending on the permeabilities.

$$\alpha = P_{CO_2}/P_{N_2}$$

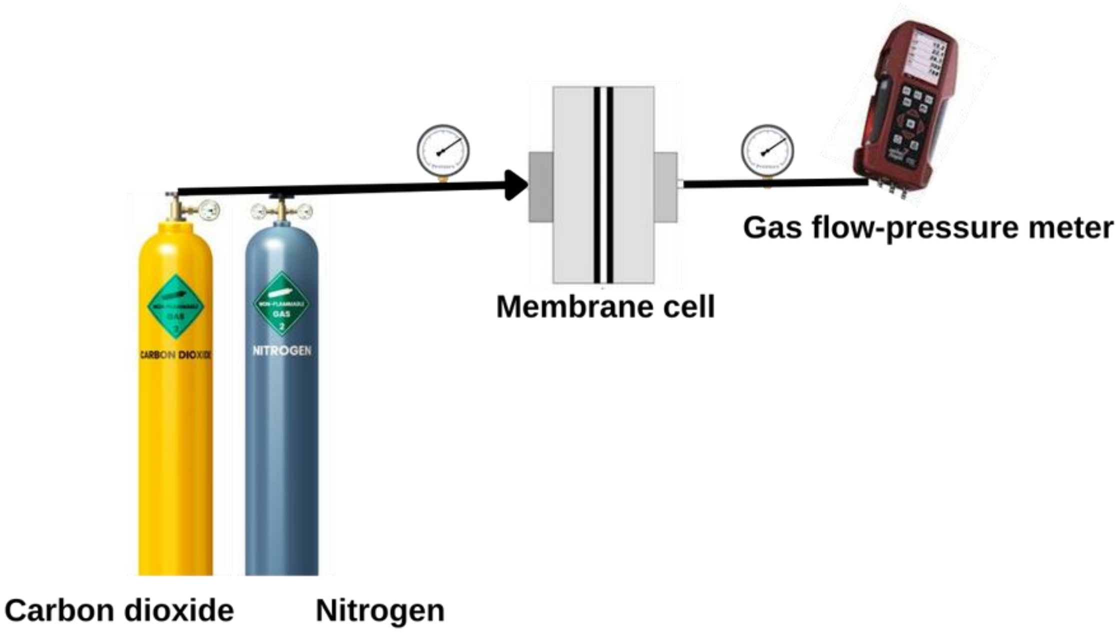

Figure 2. Schematic representation of gas permeation

2.5. Membrane Characterization

The morphology of the prepared membranes was determined by scanning electron microscopy (SEM, JEOL JSM-7100-F, covered with platinum and gold), and their bond structures were determined by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, between the wavelength of 650 cm^{-1} and 4000 cm^{-1}). Their mechanical strength was determined by stress-strain tests (ANKARIN Universal Testing machine using ASTM D882 standard). The thermal behavior of the membranes was determined by thermogravimetric analysis (TGA, Mettler Toledo) and differential diffraction calorimetry (DSC, Mettler Toledo). Both techniques were performed at a temperature rate of 10 °C/min and in a nitrogen environment. All tests were repeated at least three times, and stable results were obtained.

3. Results and Discussion

3.1. Characterization

An SEM study is essential for characterizing membranes since the primary challenge is that these structures cannot be dispersed uniformly, which is especially difficult when making nanocomposite materials. Moreover, the unselected spaces that form between the phases are another problem. Figure 2 indicates the surface and cross-sectional morphology of the MIL 140B loaded membrane. The membrane was produced smooth, pore-free, and uniformly, as shown in Figure 3.

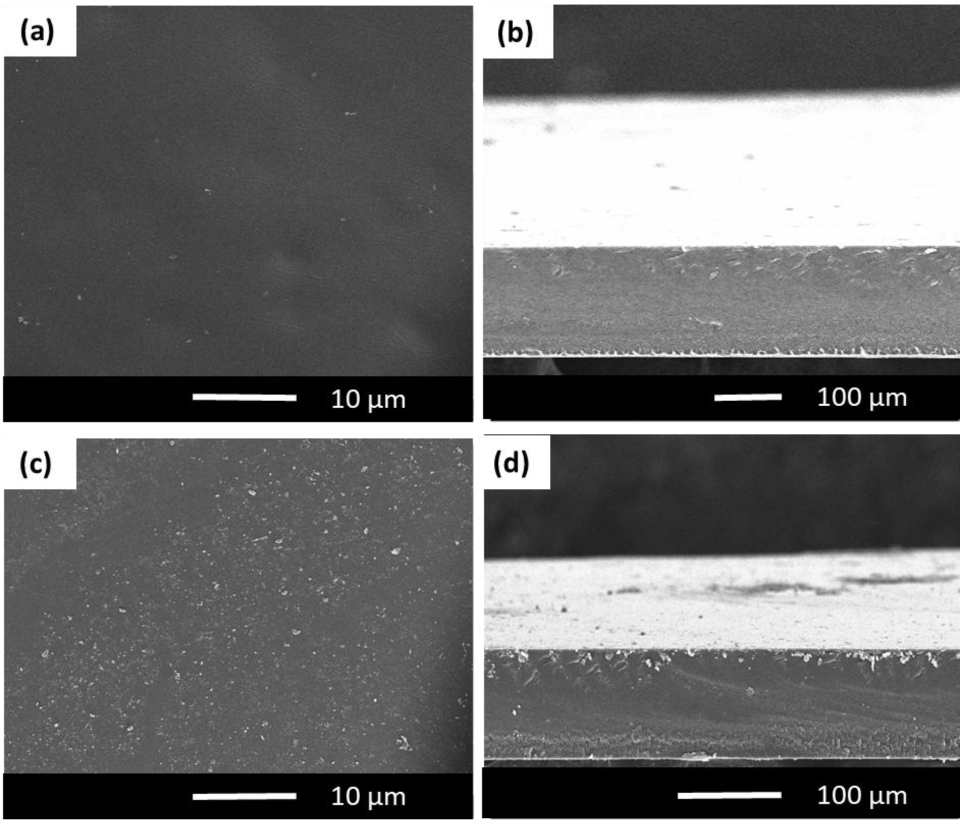

Figure 3. Surface (a) and (c) and cross-sectional (b) and (d) micrographs of pristine and 2 wt.% of MIL 140B loaded membranes

FTIR analysis of the filled and unfilled PVA membranes is seen in Figure 4. PVA membrane is shown. The graph shows some significant discoveries. One of them is that as the MIL 140B increased, the ratio of the OH vibration peaked at 3300 cm^{-1}, which is observed to be reliant on the water-moisture content, reduced. Since MIL 140B has no structural OH peaks and a lower moisture content and water-holding capacity than PVA, a decrease in OH peak intensity is expected, given the intensity of OH peaks in PVA and membrane hydrophilicity. In membranes, the stretching peaks of the -CH_3 bond were around 2900 cm^{-1} and 2840 cm^{-1}. As the MOF ratio rose, this ratio decreased once more. The aromatic component of the organic binder's C=C is represented by the peaks seen between 1420 and 1550 cm^{-1}.

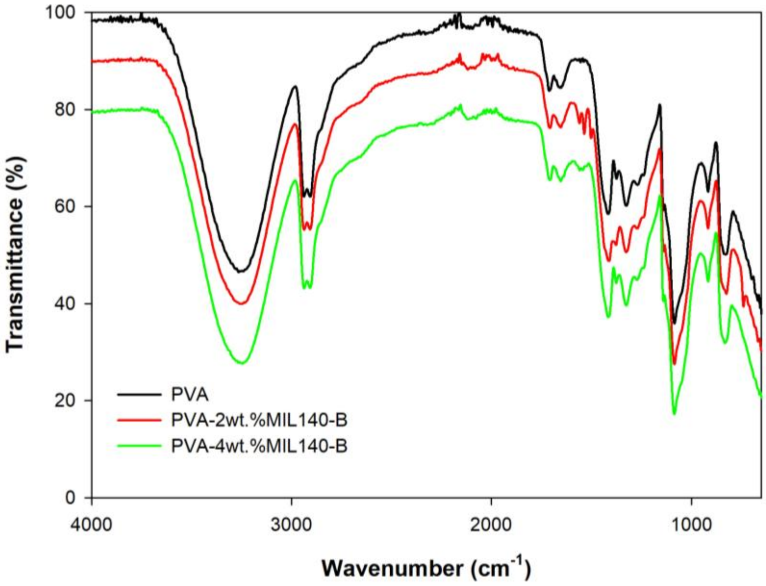

Figure 4. FTIR analysis of the filled and unfilled PVA membranes

Thermal analysis tests were applied to the PVA, 2 wt.% MIL 140B and 4 wt.% MIL 140B loaded PVA membranes. Since the gas separation process took place at room conditions, the effect of temperature is indirectly important. The TGA and DSC tests were performed to observe the change of MIL 140B additive on the structure of the polymer. Figure 5 shows the effect of MIL 140B incorporation on the degradation temperatures. According to this, MIL 140B incorporation significantly affected the thermal structure of the membrane. The degradation rate of the membrane increased, and the degradation temperatures decreased. This shows that the permeability and selectivity of the membrane will change at possible high temperatures. This may be due to removing chemicals and solvents in the MIL 140B material at different temperatures. In addition, it was seen in FTIR tests that the moisture retention values of the membrane to which MIL was added increased. For this reason, the degradation percentage may have been high.

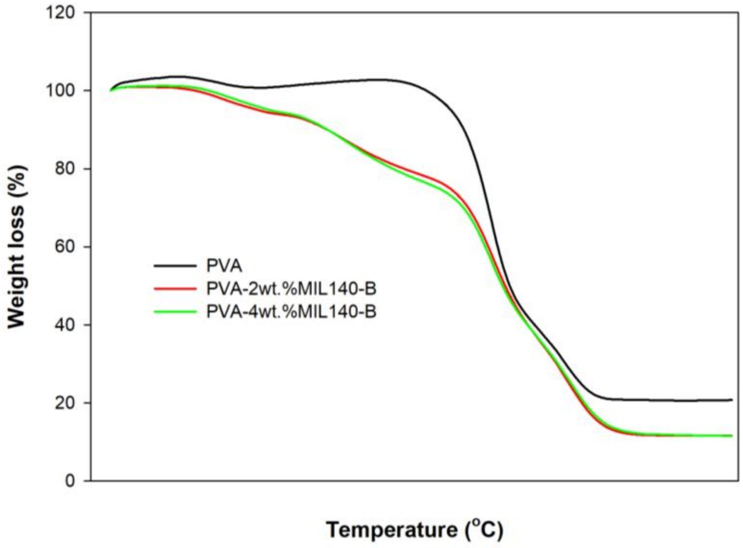

Figure 5. TGA results of the filled and unfilled membranes

Figure 6 shows the effect of MIL 140B addition on the crystal structure of the membrane. As predicted, the melting enthalpy of the polymer decreased with adding the filler. This shows that the structure is more amorphous in the nanocomposite than the pristine membrane. It has already been observed physically in membranes that the structure of MIL 140B filled membrane was more flexible. Based on this finding, it is possible to predict that the permeability of the membranes to which MIL 140B is added will increase. However, it is not possible to comment on selectivity at this stage. The melting temperature also decreased significantly.

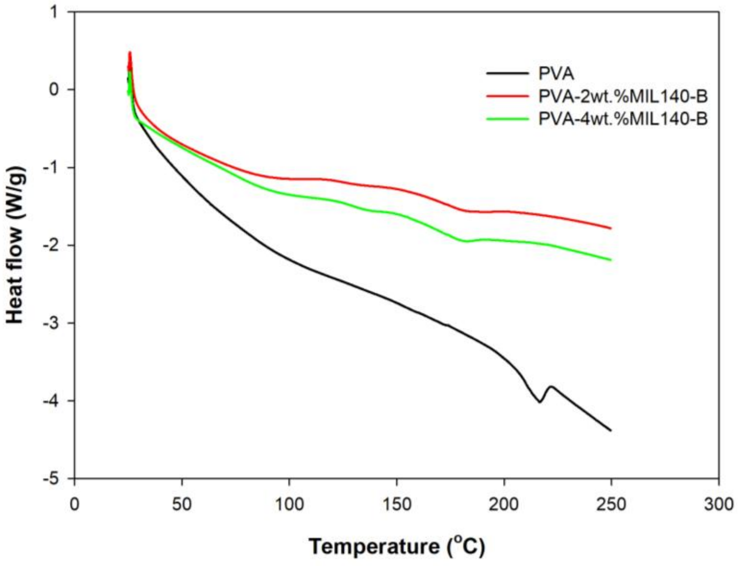

Figure 6. DSC results of the filled and unfilled membranes

Mechanical analysis tests complied with ASTM D882 standard in a laboratory-style tensile machine. The elongation at break (strain) and strength (stress) values were calculated using software based on the force values at and up to the instant of break and the elongation values from the tensile test. The values for PVA-MIL 140B are displayed in Table 1. The table indicates that adding MIL significantly increased strength. In other words, the mechanical strength increased according to the MIL material. However, a reduction was noted following the 4 wt.% loading. This is because overloading weakens the polymer-inorganic contact, causing the rupture at this location.

Table 1. Mechanical analysis of membranes

Membrane	Tensile stress (Mpa)	Elongation at break (%)
PVA	23.7	115.8
1 wt.% MIL 140B-PVA	36.7	121.4
2 wt.% MIL 140B-PVA	43.5	139.8
3 wt.% MIL 140B-PVA	47.7	181
4 wt.% MIL 140B-PVA	25.5	11.76

3.2. Gas Separation Results

At this point, pressurized gas was fed into the gas separation system along with the membranes that had been produced. The system was run continuously with varying volume and constant pressure. Prior to using mixed gases, the experiments were conducted with a single carbon dioxide and nitrogen feed, and permeability and ideal selectivity were calculated.

Initially, the effect of the MIL ratio on each membrane's performance was evaluated. 2 bars of pressure were used during these tests at room temperature. The selectivity was consistently enhanced by increasing MIL 140B, as Figure 7 illustrates. This is due to the fact that MOF particles enhance the tortuous pathway, which increases the diffusion selectivity of carbon dioxide more than nitrogen. Since MIL 140B has micropores through which carbon dioxide can pass, the permeability has also increased. Nevertheless, with a 3 wt.% loading rate, the permeability of carbon dioxide declines. Although this decrease was still higher than the pure PVA value, it can be said that overloading affects and reduces the active separation area, preventing the passage of raw carbon dioxide and nitrogen.

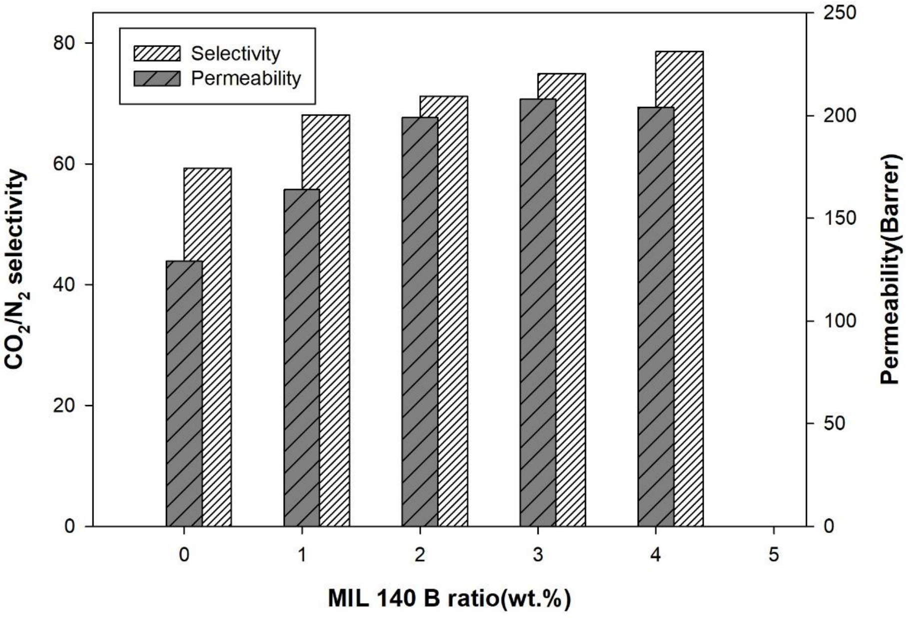

Figure 7. Effect of MIL 140B additive on PVA permeability and selectivity

Figure 8 shows the effect of pressure on the selectivity and permeability of carbon dioxide in both plain and MIL 140B incorporated membranes. There are interactions between carbon dioxide and the polymer when it is separated in a polymeric membrane. The polymer's structure and capacity for selective separation are altered due to these interactions. Particularly at high pressure, this condition—also referred to as plasticization—is more effective. Permeability and selectivity can, therefore, significantly increase or decrease when gas separation occurs at a high-pressure differential. While some polymers experience a drop in selectivity and an increase in permeability due to this interaction, others may experience the opposite consequence.

The figure shows that the permeability values of both the plain and composite membranes grew relatively slowly as the feed pressure rose, which can be viewed as a beneficial consequence. At low pressures, it is presumed that the glassy polymer (PVA) does not undergo structural breakdown and that the flow increase causes an increase in permeability. More crucially, though, the selectivity value dropped dramatically. This indicates that while the polymer's permeability to carbon dioxide rose, it increased more to nitrogen, which is undesirable. It is actually possible to argue that the membrane's capacity to separate declines as pressure rises because the percentage loss in selectivity is significantly greater than the percentage increase in permeability. The figure's most significant observation is that the composite membrane exhibits a smaller decline in selectivity. Additionally, permeability rose more. As a result, it is evident that adding MIL 140B lessens the membrane's plasticizing impact.

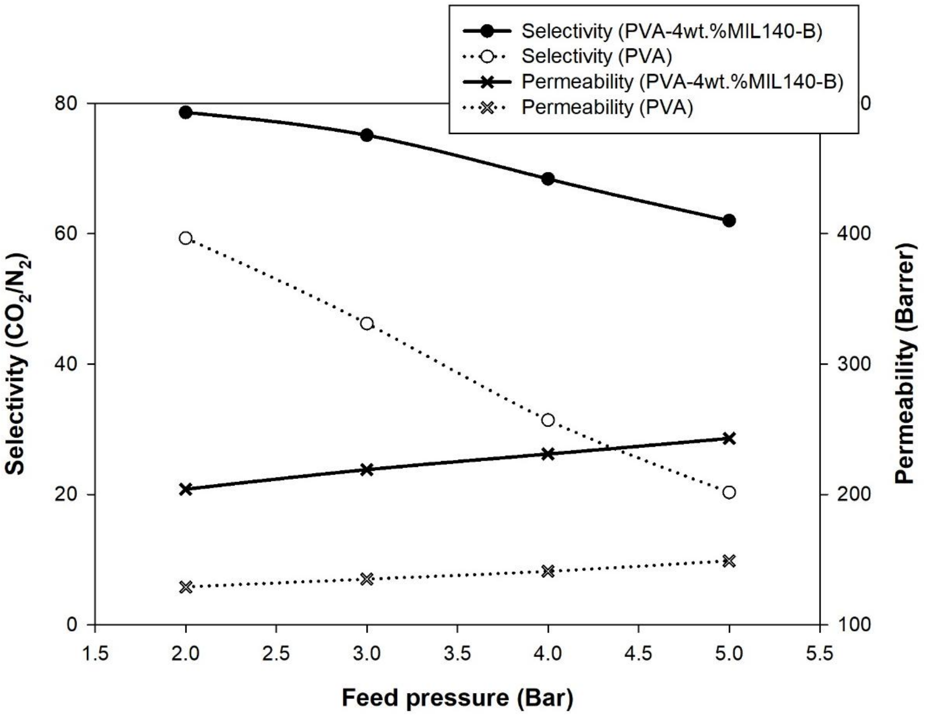

Figure 8. Effect of pressure on PVA-MIL 140 B membrane separation performance

In general, the characteristics and operating parameters of the gas and the membrane determine how a single gas permeates through them. When a gas is in a mixture, its behavior through the membrane is determined by both the gas and its interaction with the membrane and by the gas's interaction with the other gas. Consequently, using permeability data of single gases to predict the separation properties of gas mixtures can sometimes lead to incorrect conclusions. Numerous factors can influence a given situation, including variations in sorption on the membrane surface, rates of sorption, concentration polarization, plasticization, and dissolution or reactivity of gases with one another. This can often lead to a decrease in permeability in glassy polymers. This is because there is a fixed amount of sorption sites, especially in the polymer matrix, which become saturated at a certain pressure and thus decrease solubility at higher penetration pressures. This is a kind of competitive penetration. For this reason, especially in glassy polymers, it has been stated that the permeability in mixed gases is lower than in pure ones. On the other hand, if there is a carbon dioxide separation, especially at high pressure, plasticization in the medium increases the permeability.

Figure 9 shows the effect of the MIL 140B ratio on the separation performance of mixed gas (30% CO_2). The increase-decrease trends in permeability and selectivity are similar to the mixture's single gases. However, the values are lower than the single values. As mentioned above, there are many reasons for this low value. Competitive solubility and diffusion are two of them. However, it is incorrect to talk about pressure-dependent changes (plasticization). Because the study was carried out at low pressure. The figure shows that while the MIL 140B ratio increased from 0 wt.% to 4 wt.%, CO_2 permeability increased from 92 Barrer to 179 Barrer, and selectivity increased from 41.4 to 58.7.

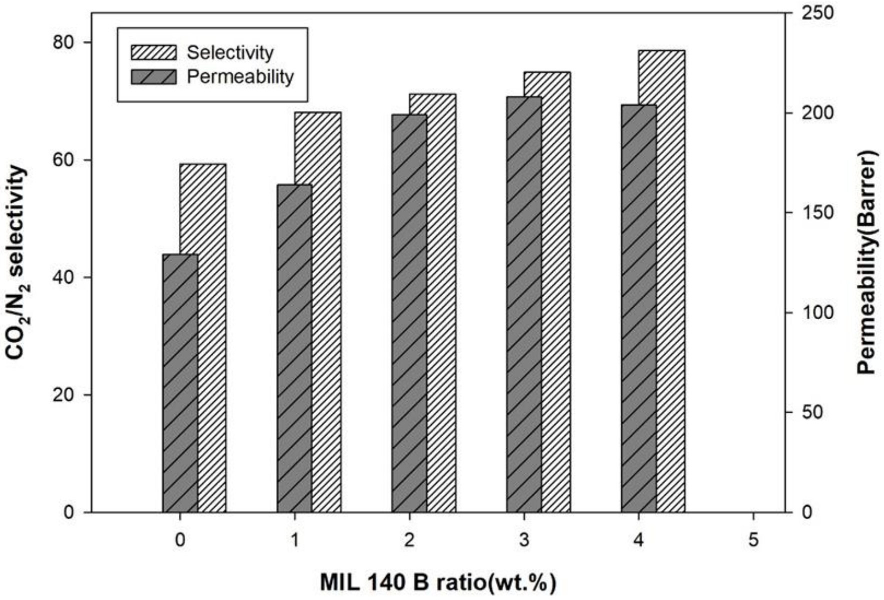

Figure 9. Effect of MIL 140B additive on PVA membrane permeability and selectivity in mixed gases

4. Conclusion

The separation of carbon dioxide from flue gases is of great environmental importance, and the success of membrane processes in this field is increasing daily. Membrane separation performance is especially evaluated in terms of selectivity. In this study, membranes with polyvinyl alcohol matrix were prepared by synthesizing MIL 140B to improve the carbon dioxide separation performance and the thermal and mechanical strength of the membrane during separation. In particular, it was observed that the thermal strength and mechanical strength of the membrane doped with 3 wt.% MIL 140B increased significantly compared to the pure membrane. In model flue gas separation studies, selectivity values above 58 were obtained. In future studies, it can be applied to the laboratory scale experimental results on a larger scale.

Author Contributions

The author read and approved the final version of the paper

Conflict of Interest

The author declares no conflict of interest.

Ethical Review and Approval

No approval from the Board of Ethics is required.

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