

# Synthesis and Characterization of Cross-linked Polyvinylalcohol/Polyethyleneglycol Blend Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation

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## Abstract:

Polymeric membrane technology has received increasing attention in the field of gas separation, e.g., natural gas sweetening [1], hydrogen recovery and purification [2], and flue gas separation [3], due to its low cost, energy efficiency and ease of operation. Natural gas sweetening aims to separate acid gas, mainly CO<sub>2</sub>, from CH<sub>4</sub> and other mixed gas components, to meet pipeline specifications (2% CO<sub>2</sub> in the U.S.A.). Currently, the polymer membranes, either commercially or reported for CO<sub>2</sub>/CH<sub>4</sub> separation in the literature, show either a high permeability with a low selectivity [4] or a high selectivity with a low permeability [5,6], which potentially restrict their scale-up application. Recently, polymer membranes containing polar ether segments have been investigated to separate CO<sub>2</sub> from CH<sub>4</sub> due to the strong affinity between CO<sub>2</sub> and polar ether segments. For example, pure acrylated PEG has been reported to fabricate cross-linked polymer membranes via UV-irradiation, and the resulting membranes showed good performance in CO<sub>2</sub>/CH<sub>4</sub> separation [1,7,8]. However, it was difficult to control the formation of large, homogeneous and defect-free ultra thin films. Also, the membranes have relatively low mechanical strength and high cost.

The objective of this research, therefore, is to develop an economically and technically viable polymer membrane for CO<sub>2</sub>/CH<sub>4</sub> separation. The target membrane should have desirable separation performance, good mechanical strength and low cost. A cross-linked polyvinyl alcohol (PVA)/polyethylene glycol (PEG) blend membrane was developed to meet the above requirements. The ethylene groups in PEG enhances CO<sub>2</sub> transport through membrane while PVA provides mechanical strength of polymer matrix. The cross-linking and entanglements of PVA and PEG create robust and homogeneous network. In order to improve separation performance, zeolite 5A was chosen as the inorganic filler due to its stronger adsorption of CO<sub>2</sub> than CH<sub>4</sub> [9].

The cross-linking time, molecular weight of PEG and PEG (MW 200) content were found to significantly affect the transport properties of the zeolite unfilled PVA/PEG membrane. The optimal cross-linking time was found to be 84 minutes in order to obtain simultaneously good CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. PEG (MW 200) showed the maximum CO<sub>2</sub> permeability among the PEGs with different average molecular weight investigated. Figure 1 shows the effect of PEG (MW 200) content on the separation performance of CO<sub>2</sub>/CH<sub>4</sub>, and it was found that, at 64 wt.% PEG (MW 200), the membranes showed good CO<sub>2</sub> permeability of 80.2 Barrers (1Barrer = 10<sup>-10</sup> cm<sup>3</sup> (STP)•cm/cm<sup>2</sup>•s•cmHg) and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 33.

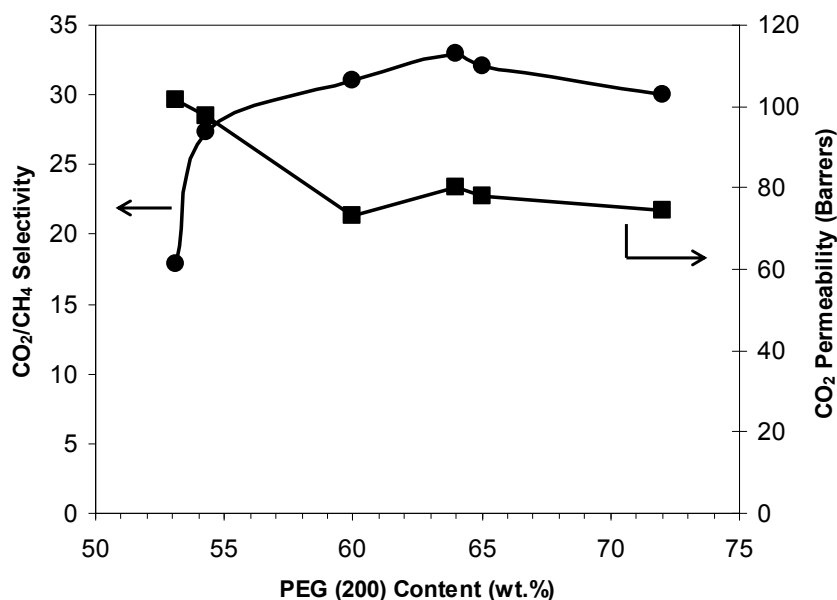


Figure 1. Effect of PEG(MW 200) content on the separation performance of CO<sub>2</sub>/CH<sub>4</sub> for the PVA/PEG membrane at 30°C and 150 psi.

The effects of zeolite 5A loading, temperature and feed pressure on the gas separation performance of both zeolite-filled and unfilled PVA/PEG membranes were investigated. Figure 2 illustrates the effect of zeolite 5A loading on CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity for the PVA/PEG membrane. As can be seen that the CO<sub>2</sub>/CH<sub>4</sub> selectivity decreased as the amount of zeolite 5A loading increased; while the CO<sub>2</sub> permeability first decreased, then drastically increased. The drop in CO<sub>2</sub>/CH<sub>4</sub> selectivity could be ascribed to the formation of interfacial cracking at the polymer-zeolite 5A interfaces, which have been evidenced by SEM pictures. The initial decrease of CO<sub>2</sub> permeability was mostly likely caused by the partial pore blockage of the zeolite by polymer chains; while the drastic increase of CO<sub>2</sub> permeability suggested that, with the increase of zeolite 5A loading, CO<sub>2</sub> molecules permeated not only through the polymer matrix, but an additional network created by interconnected zeolite 5A particles. The effect of temperature on the separation performance of both zeolite 5A filled and unfilled PVA/PEG membranes was investigated in the range of 16.4 - 40°C at the feed pressure of 150 psi. On the one hand, the CO<sub>2</sub>/CH<sub>4</sub> selectivities of all the membranes decreased linearly as temperature increased due to an increase in polymer chain mobility and thereby, diffusivity at the increased temperatures. However, compared to the zeolite-unfilled membranes, the CO<sub>2</sub>/CH<sub>4</sub> selectivity could be influenced to a lesser extent from the incorporation of zeolite particles into the polymer matrix. On the other hand, the permeability of both CO<sub>2</sub> and CH<sub>4</sub> increased as temperature increased for all the membranes. The trade-off relationship exhibited by the CO<sub>2</sub>/CH<sub>4</sub> selectivity and CO<sub>2</sub> permeability suggested that overall gas permeation in the PVA/PEG membranes follows the solution-diffusion mechanism. Thus, the gas permeability could be approximately described using the Van't Hoff-Arrhenius approach. Based on the calculation results, we could conclude that (1) the zeolite-filled PVA/PEG membrane had higher activation energy for both CO<sub>2</sub> and CH<sub>4</sub> than that of the unfilled PVA/PEG membrane, and (2) CO<sub>2</sub> always showed a lower pre-exponential value and activation energy than CH<sub>4</sub>. These results indicated that the

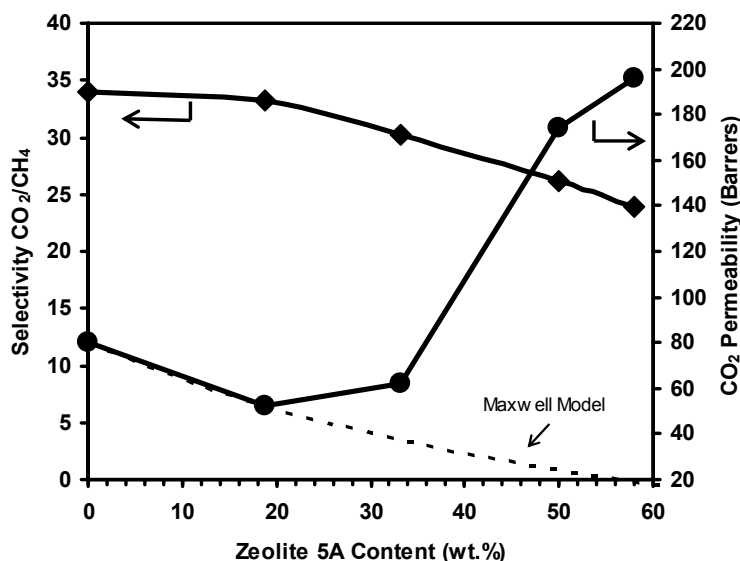


Figure 2. Effect of zeolite 5A loading content on the separation performance of CO<sub>2</sub>/CH<sub>4</sub> for the PVA/PEG membrane at 30°C and 150 psi.

temperature effect on the zeolite-filled PVA/PEG membrane was more significant than the unfilled ones, and that CO<sub>2</sub> had a lower enthalpy of sorption in the PVA/PEG membrane than CH<sub>4</sub>, possibly due to the strong interaction of CO<sub>2</sub> with ethylene oxide segments. It is noteworthy that the unfilled PVA/PEG membrane could perform beyond the Robeson's upper bound as temperature decreased. As the feed pressure increased, the CO<sub>2</sub>/CH<sub>4</sub> selectivity and CO<sub>2</sub> permeability decreased for the unfilled PVA/PEG membranes, while the filled ones were not affected significantly, indicating that the incorporation of zeolitic particles could significantly improve the performance stability of membranes at high pressures.

The separation performance results of some zeolite-filled and unfilled PVA/PEG membranes were summarized with reference to the Robeson's upper bound line for the CO<sub>2</sub>/CH<sub>4</sub> separation as shown in Figure 3. The performance of the zeolite-filled membranes approached the upper bound line with the increase of zeolite 5A loading. The performance of unfilled membranes gradually approached the bound line, and finally exceeded the boundary as the temperature decreased from 40 to 16.4°C. In comparison with the commercialized CA and Matrimid<sup>®</sup>, both the zeolite-filled and unfilled PVA/PEG membranes showed potentially to be industrially attractive.

Future work is required to eliminate or at least minimize the interfacial voids in order to improve the CO<sub>2</sub>/CH<sub>4</sub> selectivity, and reduce membrane thickness to obtain high CO<sub>2</sub> permeance at low cost.

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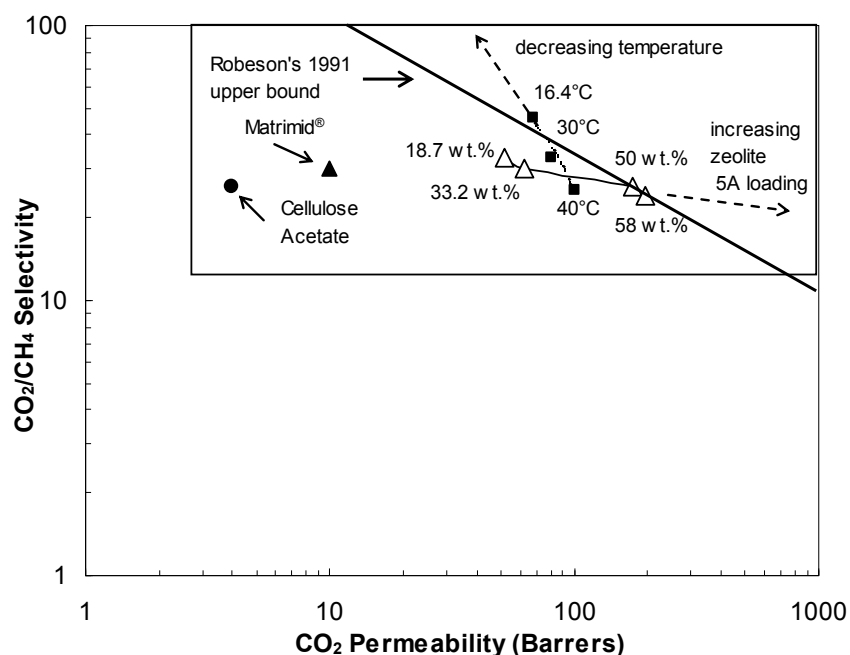


Figure 3. CO<sub>2</sub>/CH<sub>4</sub> selectivity versus CO<sub>2</sub> permeability for zeolite-filled and unfilled cross-linked PVA/PEG blend membranes. The solid line represents Robeson's 1991 "upper bound". Solid squares refer to zeolite-unfilled membranes and open triangles represent zeolite-filled membranes. The right-top shaded area is commercially attractive.

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