

CHAPTER I

INTRODUCTION

Separation technologies for carbon dioxide/methane and olefins/paraffins, particularly propylene and propane, have been expected to be developed because they currently require high investment and operating costs. The use of membrane technology is considered to be a proven technology due to its low capital cost and low energy consumption. Membrane material development is an important research area to synthesize both higher performing and more durable membranes. One of the most recent developments in the field of membrane technology is the successful commercialization of polymer membrane processes for gas separation (Ismail and Lorna, 2002).

In gas separation, a mixed gas is fed at elevated pressure across the surface of a membrane that is selectively permeable to one component of the feed. The membrane separation process produces a permeate enriched in the more permeable species and a residue enriched in the less permeable species.

The main problem of polymer membrane separation involving CO₂/CH₄ separation is plasticization. Plasticization in a polymer membrane can occur by CO₂ acting as a plasticizer. The polymer matrix swells upon the sorption of CO₂, accelerating the permeation of CH₄. As a consequence, the polymer membrane loses its selectivity (Bos *et al.*, 1999). Therefore, this phenomenon must be reduced in order to make membranes attractive to gas separation applications. For olefin/paraffin separation, the major problem of this separation is low olefin/paraffin selectivity and low olefin permeability.

Mixed matrix membranes have been developed for minimizing the plasticizing effect and enhancing gas permeability and selectivity. A mixed matrix membrane is composed of organic polymers and inorganic fillers. There are two types of mixed matrix membranes, solid-polymer and liquid-polymer mixed matrix membranes. The first is a membrane with an adsorbent embedded in the polymer phase (MMM_{ADS}). The other type of mixed matrix membrane is produced by casting liquid-adsorbent such as polyethylene glycol (PEG) and silicone rubber on a polymer

support i.e., polysulfone. Both types of mixed matrix membranes have been evaluated for the separation of polar gas from non-polar gas, e.g., carbon dioxide from nitrogen and methane as well as light paraffins from light olefins.

In a previous study, it was found that the incorporation of the solid and the liquid was effective to improve the separation performance of mixed matrix membranes. However, the gas permeation rate decreased as the components loading increased due to those components densifying the intersegmental packing of the membrane phase. In addition, it has been reported that CO₂ induced the plasticization phenomenon in which CO₂ permeance increased with increasing feed pressure. Therefore, the membranes lost their selectivity due to the CO₂ plasticization thus accelerating the permeance of CH₄ and N₂ (Soontraratpong 2005). Subsequently, Sriwasut (2006) investigated CO₂-induced plasticization and studied the suppressing plasticization for CO₂/CH₄ and CO₂/N₂ separations. Not only NaX-zeolite was coated on CA supports to form mixed matrix membranes, but it was also incorporated into cellulose acetate to form mixed matrix membrane films. Furthermore, heat treatment was considered as a means to suppress the plasticization. They concluded that the suppression of CO₂-induced plasticization has been successful for CO₂/CH₄ separation.

The purpose of this work was to investigate the performances and study the plasticization phenomenon by developing cellulose acetate mixed matrix membranes (CA MMMs) for CO₂/CH₄ and C₃H₆/C₃H₈ separation. Two types of mixed matrix membranes, solid-adsorbent and liquid/solid-adsorbent CA MMMs, were studied. NaA, CaA, NaX, NaY and silicalite were individually used as a solid adsorbent embedded in the polymer phase. Polyethylene glycol (PEG) was also used as a liquid adsorbent adsorbed into a solid adsorbent. The membrane performances for CO₂/CH₄ and C₃H₆/C₃H₈ separation were carried out using pure gas measurement at room temperature.