

## CHAPTER II

### LITERATURE SURVEY

There are many authors who studied the preparation of porous films and membranes. Islam and Dimov (1992) studied the pore formation mechanism in filled polyethylene film prepared by thermomechanical deformation. The film material consisted of high density polyethylene and SiO<sub>2</sub> as a filler. They found that the rate of deformation and the initial thickness of the film have great influence on the formation of the porous structure. When the rate of deformation increases, the crazes in the film decrease. Similarly, an increase in the initial film thickness results in a decrease in the film porosity.

Another study is the work of Kobayashi *et al.* (1993) who prepared porous polydimethylsiloxane (PDMS) membranes by catalytic hydrosilylation cure of a silicone compound. The silicone compound contained a vinyl group and a SiH. The reaction was carried out in the presence of additives such as water, ethanol, ethylene glycol, and 2-methoxyethanol. Porous structure of the membrane is formed as a result of hydrogen foams produced by the reaction between the SiH group and the OH group of the additive during cure. The porous PDMS membranes were examined for their properties as a function of the additive concentration at various cure temperatures.

One of the most important methods to prepare porous film is phase separation, also known as solution precipitation, or phase inversion. This technique, developed in 1960s, gives membranes of high fluxes and good selectivity. Lai *et al.* (1993) prepared polycarbonate (PC) membranes by wet-phase inversion process. They found that varying amounts of a non-solvent (methanol) added to the casting solution during membrane preparation increase the membrane porosity. The gas permeability of the PC membranes increases with increasing amount of non-solvent. In addition, the PC

membranes still retain good selectivity toward oxygen/ nitrogen mixtures. In the work of Matsuyama *et al.* (1999), membrane formation via phase separation induced by the penetration of water vapor was investigated. The porous membrane was prepared from Poly(vinylidene fluoride)/ dimethylformamide solution. It was found that membrane morphology changes in the order of dense, to porous (cellular), and to lacy-like structures as the humidity in the gas phase increases. They also explained membrane morphologies based on both the calculated composition paths during the process and the phase diagram.

Chitosan membranes can also be made by the wet phase inversion process (Modrzejewska *et al.*, 2001). The solvents used are acetic acid, formic acid, and citric acid. It was found that the membranes formed by this method are suitable for ultrafiltration and the best separation membrane is made from Chitosan solution in formic acid.

Besides the phase separation process, many authors have described other techniques to prepared membranes for separation purposes. A new membrane for organic liquid separation, called the filling-polymerized membrane, was proposed by Yamaguchi *et al.* (1991). The membrane was composed of two kinds of polymer materials. One was a porous substrate film, which was inert to organic liquid, and the other was a polymer, soluble only in specific solvents, filling the substrate pores. The solubility difference of the filling polymer causes permselectivity while the substrate matrix restrains the swelling of the filling polymer. The filling-polymerized membrane was prepared by the plasma-graft polymerization technique. A porous high density polyethylene film and poly(methyl acrylate) were used as the substrate and grafted polymer, respectively. Pervaporation separation of the benzene/cyclohexane mixture through the membrane was carried out. The separation takes place through the grafted polymer and the membrane shows high permselectivity for benzene.

Another good example is a cation-exchange hollow fiber membrane prepared by radiation-induced grafting polymerization of styrene onto polyethylene hollow fiber membrane and its sulfonation (Choi and Nho, 1999). Adsorption characteristics for the cation-exchange membranes were examined when the solution of  $\text{Co}^{2+}$  permeated across the cation-exchange fiber membrane. The maximum grafting peak is obtained from 70% styrene concentration at 50°C. The degree of grafting (%) is enhanced with additives such as  $\text{H}_2\text{SO}_4$  and divinylbenzene.

Gulsen *et al.* (2001) studied effects of preparation parameters on the performance of mixed matrix composite membrane made of polypyrrole (PPy) and polybisphenol-A-carbonate (PC). The mixed matrix composite membranes were synthesized to combine the good gas transport properties of conductive polymer, PPy, with good mechanical properties of PC. The parameters investigated were the effect of composition (in terms of PC content), effect of hydrophilicity or hydrophobicity of the surface, annealing, solvent evaporation temperature, and supporting electrolyte type and its concentration on the membrane performance. It was found that the most effective parameters on the membrane performance are the supporting electrolyte type and concentration. Best results were obtained for a membrane dried at 100°C which is cast from an initial solution of 7% PC, containing 0.01 M *para*-toluene sulfonic acid as a support electrolyte. The mixed matrix membrane also shows higher selectivities than dense, homogeneous, flat sheet PC membranes.

A new type of mesoporous membrane made from a material with periodic structure, MCM-48, was developed by Nishiyama *et al.* (2001). The membrane was made with a three dimensional pore structure deposited on a porous alumina support under hydrothermal conditions. They found that MAM-48 grows in the pores of alumina support and forms a composite layer of MCM-48/alumina. After calcination, the permeation of  $\text{H}_2$ , He,  $\text{CH}_4$ ,  $\text{O}_2$ ,

N<sub>2</sub>, and CO<sub>2</sub> through the MCM-48 membrane is governed by Knudsen diffusion mechanism.

Shieh *et al.* (2001) investigated the preparation and gas permeation to H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> of silicone rubber/poly(4-vinylpyridine)/polyetherimide (SR/P4VP/PEI) multi-layer composite hollow fiber membranes. It was found that dilute P4VP solutions form a defective coating layer on the top of PEI hollow fiber surface but reduce the surface porosity significantly. This makes the SR plugging feasible to regain the gas permselectivity of P4VP/PEI composite hollow fiber.

In the present study, measurement of starch contents remaining in the films is carried out using a five decimal place digital balance. In the work of Nakatsuka and Andrady (1992), thermogravimetric analysis was used as a technique to rapidly determine starch content in LDPE/starch blend films. The percent weight loss in a specified temperature range under a constant heating rate correlates well with the starch content of films in the range of 0-12 wt% starch as determined by chemical analysis. The method was used to estimate the residual starch content of LDPE/starch films, containing approximately 6 % starch, exposed under several biotic exposure conditions. They found that generally 87-88 % of the initial starch is present in the films after different types of environmental exposures.