# CHAPTER I

## INTRODUCTION

Porous polymeric membranes have gained much interest in the areas of both academic and industrial research. Because of their main advantage of low energy consumption, they are widely used in microfiltration, ultrafiltration, reverse osmosis, gas separation, and pervaporation. There are many techniques to prepare porous membranes, e.g. solution precipitation, irradiation, expanded film, and template leaching (Howe-Grant, 1993). The solution precipitation process or phase separation, developed in the early 1960s, is one of the most important methods because it yields membranes of high fluxes and good selectivity. In this process, a polymer solution is precipitated to a form membrane matrix containing pores. Lai *et al.* (1993) prepared porous polycarbonate membranes by phase separation with varying amounts of methanol added to the casting solution. The methanol added during membrane preparation was found to increase membrane porosity. Another investigation was the work of Matsuyama *et al.* (1999) who studied membrane formation via phase separation of poly(vinylidene fluoride)/dimethyl formamide solution induced by penetration of water vapor. They found that as the humidity in the gas phase increases, the membrane porosity gradually increases from dense to porous to lacy-like structures.

The phase separation technique utilizes the preparation of polymer solutions in suitable organic solvents. Therefore, this method is inapplicable to polyolefins and other polymers which do not dissolve in normal casting solvents. For this reason, many authors have described other techniques for preparing porous film from such insoluble polymers. Kobayashi *et al.* (1993) prepared porous polydimethylsiloxane membranes by catalytic hydrosilylation cure of a silicone compound containing a vinyl group and a SiH group. The curing reaction was carried out in the presence of either water, ethanol,

ethylene glycol, or 2-methoxyethanol as additive. The porous structure of the membrane is formed as a result of hydrogen bubbles produced by the reaction between the SiH group and the OH group of the additive during cure.

The most frequently used materials for making synthetic porous membranes are polyolefins. There are many reports concerning the preparation, modification, and applications of porous membrane made from these polymers. Islam and Dimov (1992) studied the pore formation mechanism in filled polyethylene film prepared by thermomechanical deformation. It was established that with an increase in the deformation rate and initial film thickness, the porosity of the membrane decreases. On the other hand, an increase in the filler content and degree of deformation results in increasing porosity.

In the present work, a new method of preparing porous polyethylene film is studied. The film matrix is prepared from a blend of low density polyethylene (LDPE) and tapioca starch. The starch particles are considered to be the dispersed, leachable component of the membrane matrix. Porous structure of films is obtained by both acidic hydrolysis and enzymatic hydrolysis of the starch particles. The morphology of the porous films is studied using scanning electron microscopy (SEM). Mechanical properties, gas permeation, and selectivity of the porous film are also investigated.

## 1.1 Film and Membrane

According to the Encyclopedia of Chemical Technology (Howe-Grant, 1993), a film is referred to a flat plastic material which has a thickness of 0.25 mm or less. Similarly, a membrane is a thin interface made from a wide variety of raw materials, from animal gut to any synthetic polymer. However, a membrane has the ability to moderate the permeation of chemical species in contact with it. Simply speaking, these two terms are

interchangeable when the material is made from plastic and used for separation purpose.

## 1.2 Types of Membrane

Membranes can be classified into 5 types: nonporous dense membranes, isotropic microporous membranes, electrically charged membranes, asymmetric membranes, and ceramic, metal, and liquid membranes, according to their physical structures. Figure 1.1 illustrates the structures of these membrane types.

### 1.2.1 Nonporous Dense Membranes

Nonporous dense membranes are dense films through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. Various components of a solution can be separated relating to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material.

### 1.2.2 Isotropic Microporous Membranes

This type of membrane has a rigid, highly voided structure with randomly distributed, interconnected pores. Usually, the pores are extremely small, in the range of 0.1-10 μm in diameter. These membranes are widely used in microfiltration and ultrafiltration.

### 1.2.3 Electrically Charged Membranes

Electrically charged membranes are membranes with fixed positively or negatively charged ions. The structure of these membranes can be dense or porous, but mostly porous with the pore walls containing charged

ions. A membrane with positively charged ions is called an anion-exchange membrane because it binds anions in the solution. Similarly, a membrane carrying negatively charged ions is referred to as a cation-exchange membrane. This type of membrane is used in electrodialysis where separation is controlled by the charge and concentration of the ions in solution.
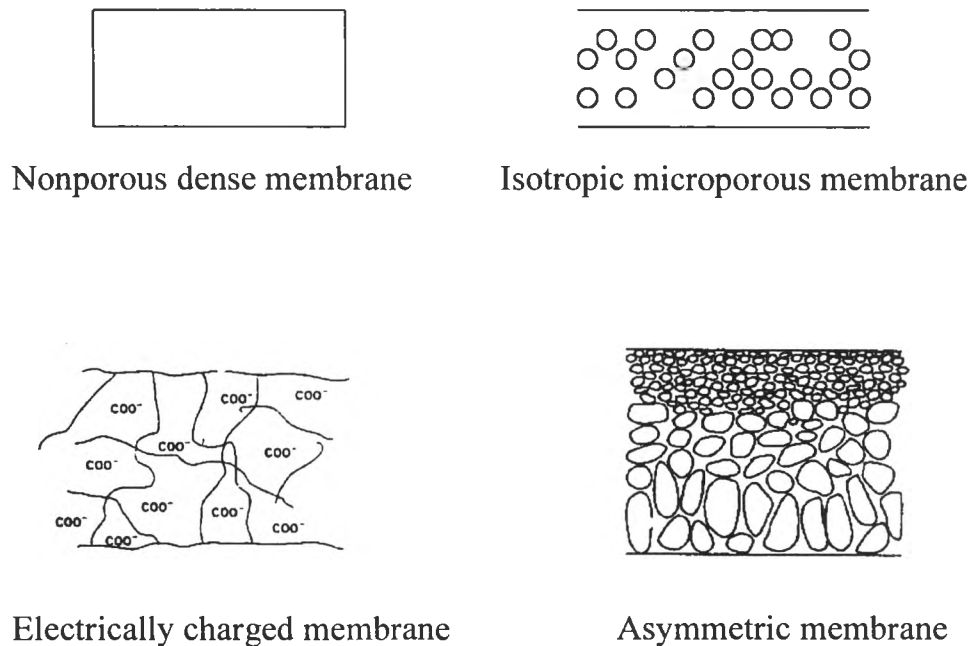


Nonporous dense membrane                    Isotropic microporous membrane



Electrically charged membrane                    Asymmetric membrane

**Figure 1.1** Schematic diagrams of membrane types.

### 1.2.4 Asymmetric Membranes

Asymmetric membranes have an extremely thin surface layer supported on a much thicker porous substructure. The surface layer and the substructure may be formed in a single process or made separately. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer. The substructure only acts as a mechanical support. This type of membrane has the advantage of high fluxes so they are used in many commercial separation processes.

### 1.2.5 Ceramic, Metal, and Liquid Membranes

Among other types of membrane, ceramic membranes are a special class of microporous membranes. They are being used in microfiltration and ultrafiltration when solvent resistance and thermal stability are required. On the other hand, metal membranes have dense, nonporous structure and are being employed in the separation of hydrogen from gas mixtures. For the case of coupled and facilitated transport processes, liquid membranes containing carriers have been developed. However, the more recent development of much more selective conventional polymer membranes has diminished interest in processes using liquid membranes.

## 1.3 Preparation of Porous Membranes

A wide variety of techniques can be employed to prepare porous membranes. Most of these methods were developed based on the nature of polymers used as raw materials. In addition, each process gives different membrane characteristics, e.g. average pore size, porosity, tortuosity, mechanical properties, and even selectivity. The main techniques usually exploited are irradiation, expanded film, template leaching, and phase separation. The first three methods give isotropic microporous membranes while the last one produces asymmetric microporous membranes.

### 1.3.1 Irradiation

This method was first developed by the Nuclepore Corp. The process has two steps. First, a polymer film is irradiated with charged particles from a nuclear reactor or other radiation sources. When charged particles pass through the film, polymer chains will break and leave sensitized or damaged tracks. Then, the film is passed through an etch solution, which etches the polymer along the sensitized nucleation tracks to form pores. In the

first step, the exposure time of the film to radiation indicates the number of pores in the film. Similarly, the etch time determines the pore diameter. This process gives membranes of uniform pore size with tortuosity close to 1.0. However, the membrane porosity is usually relatively low, about 5%, so fluxes are low.

### 1.3.2 Expanded Film

Porous membranes prepared by expanded film method are made from crystalline polymers utilizing an orientation and stretching process. In the first step, a highly oriented film is produced by extruding the polymer at a temperature close to its melting point with a rapid drawdown. After cooling, the film is stretched a second time, up to 300%, perpendicular to the original orientation direction of the polymer crystallites. This second extension deforms the crystalline structure of the film and produces slit-like pores with diameter of 20-50 nm between crystallites. The process is illustrated in Figure 1.2.
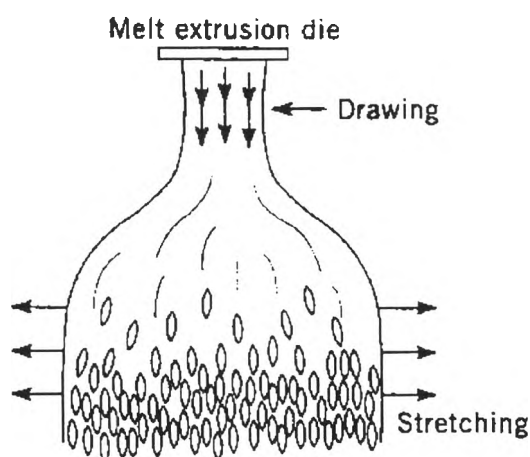


**Figure 1.2** Preparation of porous membrane by expanded film.

The original expanded film membranes had relatively poor tear strength along the orientation direction and were not widely used as microfiltration membranes. They found application as porous inert separating barriers in batteries and some medical devices. Recently, the process has been modified to produce these membranes as hollow fibers.

### 1.3.3 Template Leaching

Template leaching is a preparation method suitable for polymers which do not dissolve in common organic solvents. In this process, a homogeneous film is prepared from a mixture of membrane matrix material and a leachable component. The leachable component can be a soluble low molecular weight material or even a macromolecule such as poly(vinyl alcohol) or poly(ethylene glycol). After the film has been prepared, the leachable component is removed with a suitable solvent and porous structure is formed.

### 1.3.4 Phase Separation

This process is also know as phase inversion or solution precipitation. It is the most important porous membrane preparation method by which almost half of all microporous membranes are made. In this process, a clear polymer solution is precipitated into two phases: a solid polymer-rich phase that forms the membrane matrix, and a liquid polymer-poor phase that forms the membrane pores. Polymer precipitation from a solution can be induced by several ways such as cooling, solvent evaporation, precipitation by immersion in water, or imbition of water from the vapor phase. The membranes prepared by this method are used widely in ultrafiltration and reverse osmosis. However, the method is not suitable for insoluble polymer such as polyolefins.

## 1.4 Tapioca Starch

Tapioca starch is produced from the roots of cassava plant which grows in tropical countries from the Tropic of Cancer to the Tropic of Capricorn. The cassava plant has been classified as *Manihot utilissima* Pohl of the family *Euphorbiaceae* (Corbishley and Miller, 1984, ch.13). It is divided into two main categories: *Manihot palmata* and *Manihot aipi*, alternatively, bitter and sweet cassava. The sweet cassava has hydrogen cyanide less than 50 mg per kilogram of fresh root. Therefore, it is grown for human and animal food. On the other hand, the bitter root may contain up 250 mg or more of hydrogen cyanide per kilogram of fresh root. This bitter cassava is used for industrial raw material.

Unlike other types of starch, tapioca starch has high amylopectin content which results in relatively high molecular weight starch. In addition, it has lowest amounts of protein, lipid, and phosphorus as shown in Table 1.1.

**Table 1.1** Composition of common commercial starches (Shogren, 1998, ch. 2).

| Source of starch | Amylose (%) | Amylo-Pectin (%) | Protein (%) | Lipid (%) | Ash (%) | Phos-Phorus (%) |
|---|---|---|---|---|---|---|
| Corn | 50-70 | 30-50 | - | 1.0-1.2 | - | - |
| Wheat | 27 | 72 | 0.4 | 0.8 | 0.2 | 0.06 |
| Potato | 25 | 74 | 0.1 | 0.1 | 0.4 | 0.08 |
| Tapioca | 17 | 82 | 0.1 | 0.1 | 0.2 | 0.01 |

Since tapioca starch chains are relatively rigid and highly hydrogen bonded, the granules are insoluble in cold water but gelatinizes in hot water.

The gelatinization of tapioca starch occurs due to the formation of an amylose and amylopectin network upon melting of starch crystallites. The process takes place in a discrete temperature range called irreversible swelling temperature range. Table 1.2 shows this temperature range of tapioca starch comparing to other starches.

**Table 1.2** Irreversible swelling temperature range of starch from different sources (Kirk-Othmer, 1997).

| Source of starch | Irreversible swelling temperature range (°C) |
|---|---|
| Potato | 59.0-68.0 |
| Tapioca | 58.5-70.0 |
| Corn | 62.0-72.0 |
| Waxy corn | 63.0-72.0 |
| Wheat | 58.0-64.0 |

Tapioca starch finds application as human and animal food, paper binder, adhesives, and biodegradable plastics. Because of its low cost and high availability, tapioca starch-based plastics have much attention in the past decades. It can be used in both granule and gelatinized forms as a filler to blend with commodity plastics such as polyethylene.

In the present study, tapioca starch was used in its granule form as a dispersed phase to blend with low density polyethylene. Then, the LDPE/starch blends were extruded into thin films using film extruder. To investigate the porous film preparation process, starch particles were removed by acid hydrolysis and enzymatic hydrolysis to produce porous structure. The mechanical properties, SEM photographs, and gas permeability of the porous film were also studied.

## 1.5 Objectives

The objectives of the thesis work are:

(i)     to prepare polyethylene film containing porous structure from LDPE/starch blend

(ii)    to determine the mechanical properties of the porous film

(iii)   to determine the gas permeability of the porous film.