CHAPTER III
EXPERIMENTAL

3.1 Materials

Commercially available polyvinyl alcohol (PVA) with Mw = 108,000 g/mol and degree of hydrolysis of 99.7 was supplied from Polysciences. Calcium carbonate (CaCO₃) was from Sigma-Aldrich and boric acid, (B(OH)₃) was purchased from Merck. Distilled water was used throughout the experiment.

3.2 Equipments

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectrum (FTIR) is used to determine the functional groups of chemical composition of raw materials and composite materials. The sample preparation is carried out by mixing fine powder of sample with KBr powder by using a spectrophotometer in a range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

3.2.2 Thermogravimetric Analysis (TGA)

Thermogravimertric analysis is used to determine thermal stability of PVA, CaCO₃ and porous hybrid materials by Perkin Elmer Thermo gravimetric/Differential Thermal Analyzer (TG-DTA). Approximately 2-8 mg of samples was analyzed at a temperature range from 25 to 900 °C in a dynamic nitrogen atmosphere with a flow rate of 20 ml/min and a heating rate of 10 °Cmin^{-1}.

3.2.3 Scanning Electron Microscope (SEM)

Microstructure and surface morphology of porous composites are observed by a scanning electron microscope (SEM). The specimens were coated with gold under vacuum before observationto make them electrically conductive.

3.2.4 LSI Lyophilization/ Freeze Dryer

A freeze dryer was used to fabricate organic-inorganic porous hybrid composite.

3.2.5 Ultrapycnometer1000 (He-Pycnometer)

The skeletal density of polyvinyl alcohol/calcium carbonate porous hybrid composite was characterized by a helium gas pycnometer (Quantachrome, USA). The helium gas was purged through the sample with a pore inside to obtain the volume of gas and was calculated with the mass of the sample.

3.2.6 Surface Area Analyzer (Autosorp-1MP)

The pore structures of hybrid composites relating to surface area, pore volume, and pore size distribution are obtained by measuring their nitrogen adsorption–desorption isotherms at-196 °C (Autosorption-1MP, Quantachrome, USA).The specific surface area (S_{BET}) was calculated by the linear equation of Brunauer-Emmett-Teller (BET).

3.2.7 Gas Separation Unit

CO_2 (HP, Prax Air) and CH_4(99.999%, Alternative Chemical) were used as a testing gases. The experiments set up were carried under room temperature and the pressure different across membrane was maintained at 10 psi. The testing gas was measured by using a universal gas flow meter (ADM 1000).

3.3 Experimental Procedures

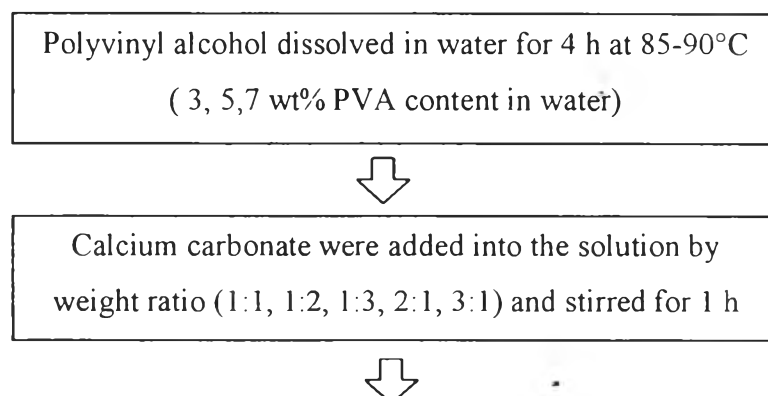### 3.3.1 Preparation of Polyvinyl Alcohol/Calcium Carbonate Porous Hybrid Composite

Polyvinyl alcohol 0.3 g dissolved in 10 g of water (3, 5, 7% wt in distilled water) at the temperature in between 85-90°C 4h under continuous magnetic stirred until the completely dissolution of polymer then adding calcium carbonate by varies weight ratio of $PVA:CaCO_3$ (1:1,1:2,1:3,2:1,3:1) and stirred until homogenized mixture for 1 h.
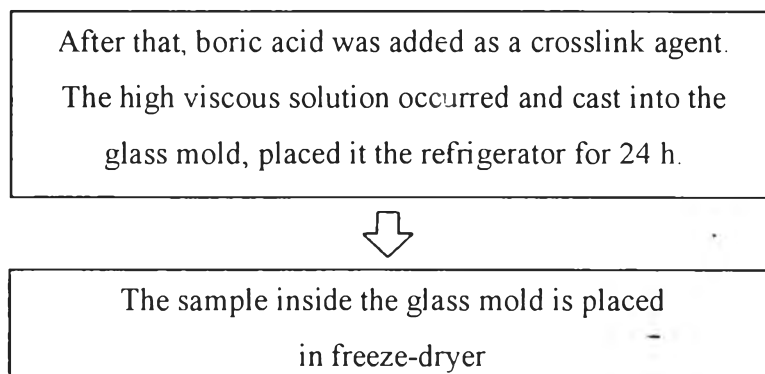
The boric acid as a cross-linking agent was dropped into the solution (1M , 1 ml boric acid in water). The solution became high viscosity and placed it into the mold. The hybrid composite solution was kept in refrigerator at 4°C. follwed by placing in freeze-dryer.

Table 3.1 PVA concentration in water and weight ratio of PVA:CaCO₃

Content of PVA (g) in water (g)	Weight ratio of PVA(g):CaCO₃(g)
0.3/10	1:1
	1:2
	1:3
	2:1
	3:1
0.5/10	1:1
	1:2
	1:3
	2:1
	3:1
0.7/10	1:1
	1:2
	1:3
	2:1
	3:1

Flow Chart of Preparation of Polyvinyl Alcohol/Calcium Carbonate Porous Hybrid Composite

Polyvinyl alcohol dissolved in water for 4 h at 85-90°C
(3, 5,7 wt% PVA content in water)

⬇

Calcium carbonate were added into the solution by weight ratio (1:1, 1:2, 1:3, 2:1, 3:1) and stirred for 1 h

⬇

> After that, boric acid was added as a crosslink agent.
> The high viscous solution occurred and cast into the
> glass mold, placed it the refrigerator for 24 h.

⇩

> The sample inside the glass mold is placed
> in freeze-dryer

Figure 3.1 Preparation flow chart of PVA/CaCO₃ porous composite.

3.3.2 Characterization Hybrid Porous PVA/CaCO₃ Composite

In this part, the samples after freeze-dried were tested the functional group of the composite by using Fourier transform infrared spectroscopy (FT-IR) from Thermo Nicolet Thermal analysis was characterized by using Perkin Elmer Thermogravimetric/Differectial Thermal Analyzer (TG-DTA) under nitrogen atmosphere with heating rate 10°C/min. Porosity of porous PVA/CaCO$_3$ composite were measured by N$_2$ adsorption/desorption isotherm and Quantachrome, Ultrapycnometer1000 (He- Pycnometer) in order to obtain surface area, pore volume and. Surface morphology of porous materials suitable for application was studied from Scanning electron microscope (SEM).

3.3.3 Gas Separation Experiment

The single-component gas permeation experiments through the porous hybrid composite. For single gas study, the testing gas was flowed for 1 hour to get equilibrium state under room temperature. The CH$_4$ or CO$_2$ was fed to the upper side of stainless steel with pressure different across sample of about 10 psi. The area of a disc shape sample that contact with the gas was 0.53 cm^2. The flow rate was measured by using an ADM 1000 universal gas flow meter, Agilent technology. The permeance of the membrane was calculated using Eq. (1). A schematic diagram of a gas separation unit is shown in Figure 3.2.

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{A \times (\Delta P) \times 76} \tag{1}$$

Where; $\left(\frac{P}{\delta}\right)_I$ = permeance of gas 'i'(GPU)

[1 GPU = 1 × 10⁻⁶ (cm³ (STP))/(cm² s cmHg)]

P = permeability of gas 'i' (10^{-10} cm3 (STP) cm/ cm² s cmHg)

[1Barrer = 10^{-10} cm3 (STP)cm/ cm² s cmHg = 7.5×10^{-18} m² s⁻¹ Pa⁻¹]
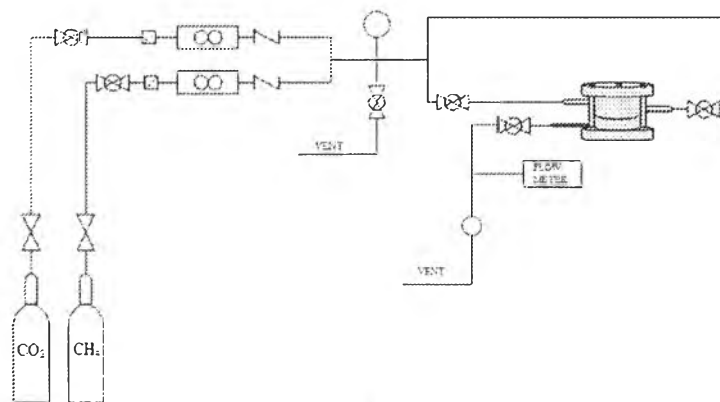
δ = thickness of membrane (μm)

Q_i = volumetric flow rate of gas 'i' (cm²/sec)

A = membrane area (cm²)

ΔP = pressure different between the feed side and permeating side (psi)

The ideal gas separation factor (Gas selectivity, $S_{A/B}$) for the component A and B is defined as the ratio of each component as shown in Eq. (2)

$$S_{A/B} = \frac{P_A}{P_B} \tag{2}$$

Figure 3.2 A schematic diagram of gas separation unit