

CHAPTER II

LITERATURE REVIEW

2.1 Organic-Inorganic Hybrid Materials

In general, the composite materials made from the natural substances for long time ago, which the combination of two materials together in order to get better properties than the conventional materials because of their limitations. The composites could show improved for the availability of many applications.

Composites are composed of at least two components in nano- or macro-molecular scale. Most of the mixture is the organic combined with an inorganic in the nature called polymer/inorganic or organic/inorganic composites (Kickelbick, *et al.*, 2007). Generally, the simplest incorporation of organic polymer and inorganic fillers are blending or mixing process with combining advantages of the composites as shown the properties of both organic and inorganic materials. Moreover, in the word hybrid composite are becoming commercially significant by the following reasons; designed material with specific characteristics, economic benefits by using filler as diluting in the expensive materials and enhance mechanical or functional properties.

The organic/inorganic composites are more interesting in a lower environmental impact replaced of traditional materials by non-toxic and bio-sources materials. Moreover, there are widely used for the reason that the polymer based composites have the numerous material variables combination contributed to stiffness, dimensional stability, low cost of raw materials, high strength, high mechanical strength and light weight (Wang, *et al.*, 2013).

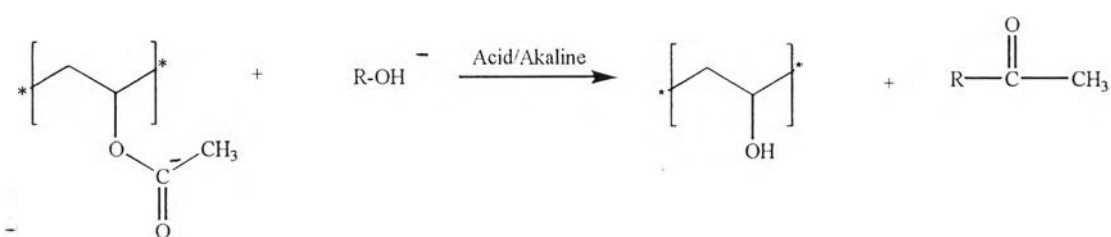
2.2 Polyvinyl alcohol (PVA)

2.2.1 Introduction of Polyvinyl Alcohol

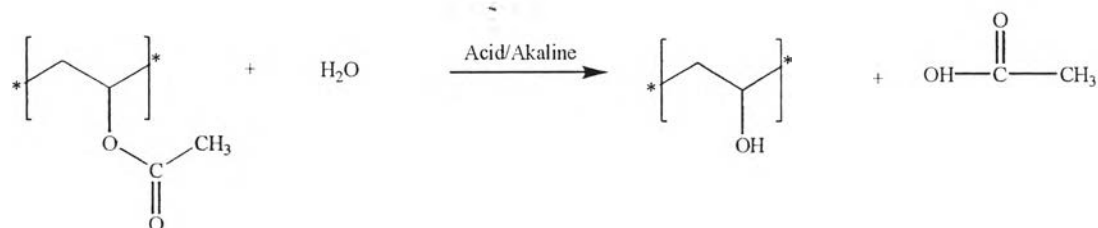
Polyvinyl alcohol (PVA) is a hydrophilic synthetic polymer which can be prepared by polymerization of vinyl acetate monomer such as transesterification, hydrolysis and aminolysis (Finch, 1992). However, the

polymerization process does not fabricate directly from vinyl alcohol monomer because of the instability. The properties of vinyl alcohol depend on the degree of polymerization and hydrolysis (Reis, *et al.*, 2006). Figure 2.1 shows the different ways of polymerization of polyvinyl alcohol from vinyl acetate by hydrolysis.

Transesterification :



Hydrolysis :



Aminolysis :

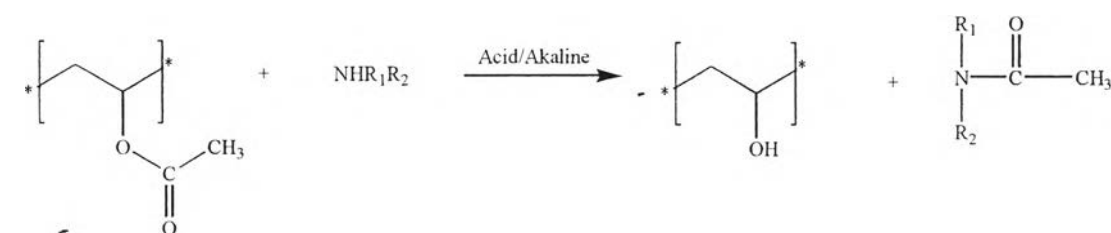


Figure 2.1 The polymerization of polyvinyl alcohol from polyvinyl acetate (Finch, 1992).

2.2.2 Properties of Polyvinyl Alcohol

Polyvinyl alcohol is an environmental polymer, the chemical structure containing the hydroxyl groups' influence on physical properties such as water soluble, biocompatible, non-toxicity. The physical properties, however, depend on the degree of polymerization, as mentioned above; can be controlled by time, temperature, additives and catalysts. Figure 2.2 shows the properties depending on its molecular weight and percentage of hydrolysis. In addition, the solubility in

water of PVA depends on the temperature. Heating to 80°C is required to dissolve completely of PVA as shown in Figure 2.3 (Finch, 1992).

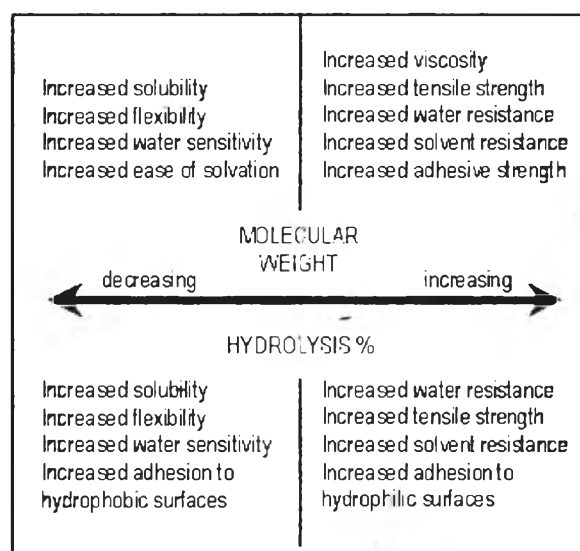


Figure 2.2 The properties of polyvinyl alcohol depend on the molecular weight and hydrolysis level. (<http://www.azom.com/article.aspx?ArticleID=266>).

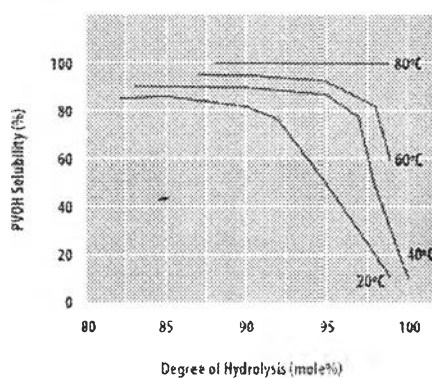


Figure 2.3 The temperature influence on the solubility of PVA in water (Finch, 1992).

2.2.3 Application of Polyvinyl Alcohol

Polyvinyl alcohol is versatile polymers which can be applied to many applications, for example, textile, paper, coating, glue. Nowadays, the popular application of polyvinyl alcohol focused on biomedical application due to its

biocompatibility, non-toxicity, biodegradable and inexpensive. The applications include controlled drug release, contact lens, tissue engineering, etc. (Bajoait, *et al.*, 2006) Moreover, for improving mechanical and thermal characteristics, polyvinyl alcohol-clay composite was studied to compare pure PVA (Ali, *et al.*, 2012)

2.3 Calcium Carbonate (CaCO_3)

Calcium carbonate is the third most abundant material on earth which is the composite of limestone which can be used as mineral filler or pigment in large quantities for the manufacturing of plastics, rubbers, coating, textiles and paper industries. Beside, calcium carbonate is also known to have bioactivities such as cell compatibility tissue compatibility and biodegradable properties because calcium carbonate plays important role in various natural organic cells such as shells, egg shells, nacles (Zheng, *et al.*, 2008 and Houmard, *et al.*, 2009). Calcium carbonate can be divided into two types; natural calcium carbonate from chalk or limestone and the precipitation of calcium carbonate (Saravari, 2003). In comparison the natural calcium carbonate provides higher purity and appears to be whiter than the one from the precipitation of calcium carbonate (Lutz, *et al.*, 2001).

Generally, inorganic mineral including talc, mica, wollastonite and calcium carbonate. Calcium carbonate is widely used in the organic/inorganic composite (Olad, 2008 and Choi, 2013) because it has low cost, high impact properties and deformability. Leong, *et al.*, (2004) studied the mechanical and thermal properties of the incorporation between calcium carbonate (CaCO_3), talc and polypropylene hybrid composite. The results explained that the viscosity of polymer melts increases with the addition of fillers. Also, by increasing of crystallinity of the PP matrix brings about an increase in the modulus. Moreover, CaCO_3 filler played an important role in increasing the impact strength of hybrid composites. CaCO_3 has been known to impart toughness to the PP matrix.

Zheng, *et al* (2008) studied the preparation of polyvinyl alcohol and calcium carbonate was prepared by a subsequential method involving in situ of CaCO_3 in PVA solution. The mechanical testing by compression press showed compression strength increased with increasing concentration of calcium carbonate.

Wang, *et al* (2013) prepared highly filled of talc and CaCO_3 in PVA composites by melting process. The results showed that not only both of two fillers were well dispersed in the PVA matrix but also the mechanical properties were improved.

2.4 Drying Methods for Porous Materials

Porous materials are the presence of pores (holes) in a solid material which can be classified into four different basics: First, interparticle and intraparticle on the basis of their origin. Second, micro-(< 2 nm), meso-(2-50 nm), macro-pores(>50 nm) on the basis of their size. Third, open and closed pores on the basis of their state. The last is rigid and flexible pores based on their strength (Inagaki, 2009). Porous materials are more interesting in various fields such as separation, catalysis, sensor, biological application, tissue engineering and purification.

The various methods have been used to prepare porous materials including gas-forming foam, three-dimensional printing, thermal-induced phase separation, electrochemistry, and drying. The drying method is proper due essential to the use of cheap and non-toxic solvent media (Wu, *et al.*, 2010). For removing the solvent, there are three different drying methods: supercritical drying, subcritical drying or ambient drying, and freeze drying (Calvo, *et al.*, 2011). Firstly, supercritical drying is the elimination of the solvent that replaced by CO_2 under the high temperature and pressure. This process is expensive but preserves the pore structure and no shrinkage occurs. Secondly, the evaporation of the solvent under ambient condition, the solvent inside the pore evaporates and then the partial pore structure will be collapsed due to the capillary force. Subcritical drying is cheaper; however, this method involves the solvent exchange in order to a lower surface tension to reduce solvent the pore destruction. Thirdly, freeze drying or lyophilization, it gets rid of the solvent by sublimation. Sublimation takes place after a frozen liquid directly move out in the gaseous state. Porous structure can be formed by the removal of frozen solvent. Typically, water is environment-friendly solvent and easy to remove the ice crystal as porogen (Qian, *et al.*, 2011). Figure 2.4 demonstrates the different ways to remove the solvent (Calvo, *et al.*, 2001).

Freeze drying has been used for organic porous materials which remain porous in many applications including the food, pharmaceutical, stabilization of living materials, preservation, and other items damaged by water.

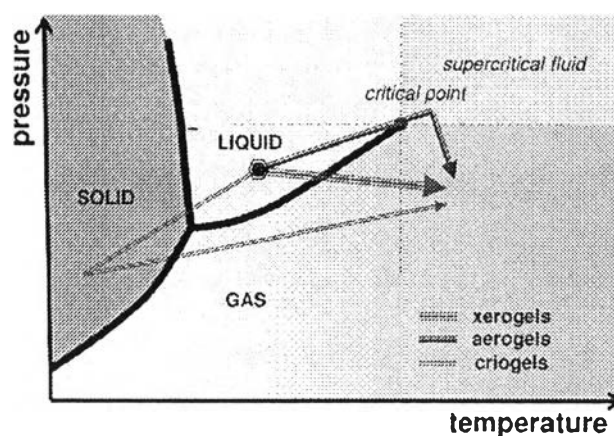


Figure 2.4 Scheme of different methods removal of solvent.

Bandi and Schirald (2006) investigated clay aerogel/PVA nanocomposites through the freeze drying process of clay generated aerogel. Aerogel clay (0.5-4 wt%) were dispersed in water for 1 h and then 10w%t PVA were dissolved in water at 90°C under vigorous stirring. SEM images of the change in morphology into the lower density and high aspect ratio on monoliths clay aerogel after freeze drying as shown in Figure 2.5. Besides, glass transition temperature (T_g) values in composites showed the behavior of clay/polyvinyl alcohol composites were higher than the matrix. However, the glass transition behaviors are a function of size, loading, dispersion of clay in polymer matrix.

In 2012, Nie and coworker studied porous composite of polyvinyl alcohol/biphasic calcium phosphate (BCP) as scaffold for bone tissue engineering by using a freeze drying method. The FE-SEM pictures of cross-sectional porous scaffolds showed in Figure 2.6. In addition, an increase in PVA content caused the pore size to decrease. The pore size has in between 50-700 μm and the porosity is 73-87%.

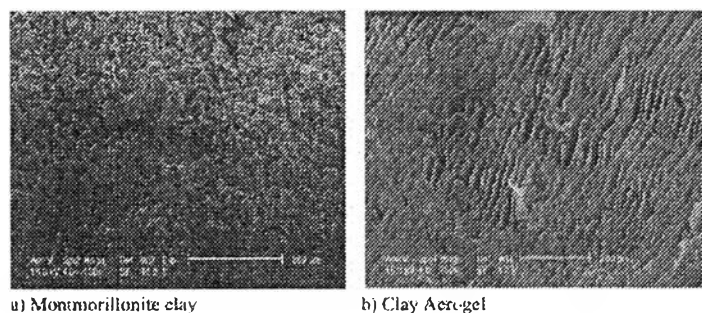


Figure 2.5 SEM images of (a) clay and (b) clay aerogel

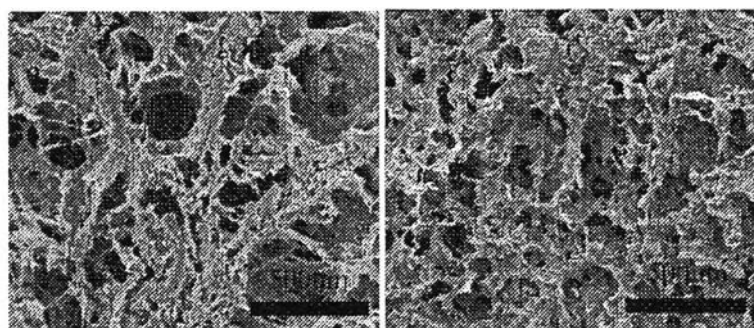


Figure 2.6 FE-SEM image of porous PVA/BCP scaffold , PVA30% (left) and PVA 40% (right).

Kumar *et al* (2012) synthesized porous composite from methylcellulose/polyvinyl alcohol by using freeze-drying process. The result explained that the porosity of porous composite was about 86% and these composites could be used in biomedical fields.

2.5 Boric Acid as a Crosslink Agent

Cross-linking is a common way to develop the performance for various applications which process of joining two or more molecules together. Crosslinking agent, firstly, was discovered by Charles Goodyear which made the stronger rubber by heating in the sulfur (Coran, 2013). Crosslinking agents are composed of at least two reactive functional end groups that can be hydroxyl, primary amine, carbonyl

and carboxylic groups. Crosslinkers are commonly used to modify or to assist of the neighboring chains of polymer to form three-dimensional structure.

In 2006, Plieva and coworker studied macroporous PVA crosslinked with glutaraldehyde. They used the crosslinking reaction under acidic conditions at a sub-zero temperature of -18°C overnight. For a good crossinking agent is glutaraldehyde or formaldehyde used under sulfuric acid or hydrochloric acid. However, the amounts of toxic residue become undesirable due to the time-consuming extraction and environmental pollutions (Hassan, *et al.*, 2000).

Boric acid can be dissolved in water which reacts with the hydroxyl groups of polyvinyl alcohol via a condensation reaction to form a gel as shown in Figure 2.7. The schematic represented for PVA and boric acid through the didiol complex and it can be changed into borate under pH about 9. The solubility of boric acid in water increases with the temperature (Smith, *et al.*, 1992). An amount of boric acid is added for developing the physical properties such as mechanical strength and water resistance.

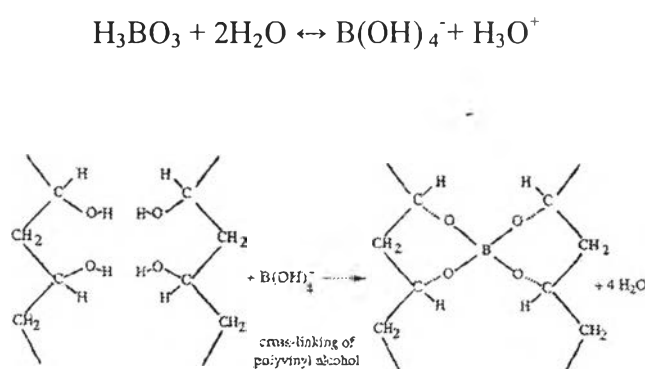


Figure 2.7 Boric acid in water and the crosslinked polyvinyl alcohol.

Maerker *et al* (1986) reported the effect of complex formation of polyvinyl alcohol and sodium borate influence on the viscosity of its solution. Furthermore, Wang *et al* (1999) synthesized polyvinyl alcohol gel with boric acid. They prepared from polyvinyl alcohol and the mixed solvent (dimethyl sulfoxide and water). The result showed the viscosity of PVA increases not only with increasing boric acid content, but also increased with temperature between $70-100^{\circ}\text{C}$. The degree of

polymerization PVA increases with increasing boric content result in higher viscosity and high Younger modulus. However, using DMSO as a solvent of PVA it cannot use in the medical fields due to its toxicity.

Further, Barros *et al* (2006) prepared polyvinyl alcohol and boric acid in the 1:1 ratio by condensation reaction as a preceramic precursor. They found that the formation of PVA-boric was easily in this reaction used low temperature route for ceramic material. The thermal stability of PVAB precursor presented better than PVA due to its cross-linking characteristic associated with the best thermal resistance of B–O compared to C–O bonds.

2.6 Gas Separation

2.6.1 Gas Emission and Membrane Separation Technology

The separation of carbon dioxide (CO₂) from methane (CH₄) plays role important for industrial process of natural gas and landfill gas treatment. Typically, natural gas is composed of 70-90% CH₄ and 1-8% CO₂ (Brunetti, *et al.*, 2014). These gases have an influence on the climate change which rising the earth's average temperature by emission into the atmosphere. CO₂ is an acidic gas, which frequently found in the natural such as gas streams, combustion of fossil fuel leading to corrode in the pipeline at presence of water and storage system in transportation and turn down the amount of energy content of natural gas (Zhang, *et al.*, 2013). Moreover, the specific CO₂ concentration for pipeline normally required lower than 2% (Othman, *et al.*, 2009).

For removal of high CO₂ concentration, it is an essential to reduce the pipeline corrosion, increase high-purity energy products (Adewole, *et al.*, 2013). There are various techniques for gas separation, including traditional absorption, cryogenic distillation, adsorption, and membrane separation. Separation of gas through membrane technology has advantages over the traditional techniques due to low energy consumption, economic, ease of process, safety environment and low maintenance requirement (Sridhar,*et al.*, 2007). Compared to other processes they have limitations, for example, absorption process is usually for gas transfer through basic solvent which this solvent can be caused corrosion in the process. An

adsorption process should be used high surface area solid materials and have high regenerability. Cryogenic process for separating gas uses low temperature with supported by large refrigeration condition, but a high energy requirement. Moreover, it cannot be used for low concentration of CO₂ (Shimekit, *et al.*, 2012).

2.6.2 Membrane Separation Materials

The concept of membrane can be described as a selective barrier between two phases where the driving force by different pressure facilitated transport can occur (Zhang, *et al.*, 2013). For gas separation through membrane materials, this technique becomes an important for CO₂/CH₄ separation process. In general, based on the morphology materials, three types of membrane can be classified: dense, asymmetric and composite. Dense membrane is typically a thin film of polymer (organic) layer whereas asymmetric combines with dense layer on top supported by porous layer. Composite membranes contain different material to make layers (Şen, *et al.*, 2007). Further, based on the materials, membrane can be divided into three categories: polymeric, inorganic and organic-inorganic membrane (Iarikov, *et al.*, 2011). The process of separation by using organic membrane can be further classified into porous and nonporous. A porous membrane is as a kind of conventional filter which have a highly voided structure, rigid, and interconnected-pores. Nonporous or dense membrane separate gases by the permeance dissolve and diffuse through in membrane.

Polymeric membranes are usually dense membranes which are low cost and easy to process. Gas permeation is based on the solution-diffusion mechanism. This is explained by solubility in the membrane and diffusion through the membrane matrix. Furthermore, they also described by glassy or rubbery membranes that operation is upon the glass transition temperature (Scholes, *et al.*, (2012). and Houde, *et al* (1996)) studied dense homogeneous cellulose acetate (CA) membrane at 35°C with different pressure. The results showed CO₂ is much more permeable than CH₄ due to the smaller kinetic diameter of CO₂ molecules had an effect on a higher solubility and diffusivity. The pressure was raised with decreasing of CH₄ permeability but increasing permeability of CO₂. Plasticization effect caused by an increasing of pressure led to increasing of free volume and chain mobility of

polymer. The CO₂/CH₄ selectivity decreases with increasing the total pressure and CO₂ concentration of feed mixture.

Li *et al.* (1998) studied blending of poly(ethylene glycol) (PEG)/cellulose acetate (CA) membranes for gas separation. The solubility coefficients of CO₂ were reduced by blending PEG2000. The containing of PEG2000 showed high diffusivity coefficients, resulting in high permeability coefficient of CO₂ compared to pristine CA. Due to the flexible main chain of PEG in amorphous domains permitted the large penetrants and easily diffuse through membrane.

Kim *et al.*, (2001) prepared pore-filled membranes by using polyacrylonitrile membrane as a support and methoxy poly(ethylene glycol) acrylate as a filler. The gas separation achieved high CO₂/N₂ permselectivity (32.5) but low CO₂ permselectivity (5.65×10^{-4} Barrer) at temperature 30 °C

Sadeghi, *et al.*, (2009) studied the effect of nano-particle incorporated in polybenzimidazole (PBI) by sol-gel method in order to enhance the gas permeability with the condition of 20 bar and 25 °C. The results showed that the incorporation of silica particles in polymer matrix increase in the polar OH groups as induced the permeability of CO₂ via solution-diffusion mechanism from 0.025 Barrer in pure polymer to 0.11 Barrer in 20wt% silica in polymer matrix.

Semsarzade, *et al* (2013) studied polymer-inorganic membrane to improve performance in terms of mechanical, thermal stability and gas separation. They prepared membrane by using silica particles incorporated with PVA in order to increase the polar groups on the surface into polyurethane. The results showed the permeability of CO₂ at temperature about 25 °C is significantly higher than other gases (CH₄, O₂, N₂) due to related on small kinetic diameter and more interaction of polar gas with polar hydroxyl group in polymer. Moreover, increasing in silica content led to increasing of gas permeability of CO₂ but low permeability of CH₄, O₂ and N₂.