CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Eggshell

2.1.1 Introduction of Egg

Egg is a product from poultry, such as hen, duck, bird etc. It is an important ingredient for food, pharmaceutical, and other applications. Egg consists of yolk, albumen, and eggshell with the composition of approximately 31, 58, and 11%, respectively, of the total weight of the egg, as shown in Fig. 2.1. (Board, *et al.*, 1994) Chemical compositions of yolk and albumen are water and organic matter, such as protein, lipid, and carbohydrate, which are high value for products. However, eggshell is a waste, mainly composing inorganic matter. (Swanson, 2011)

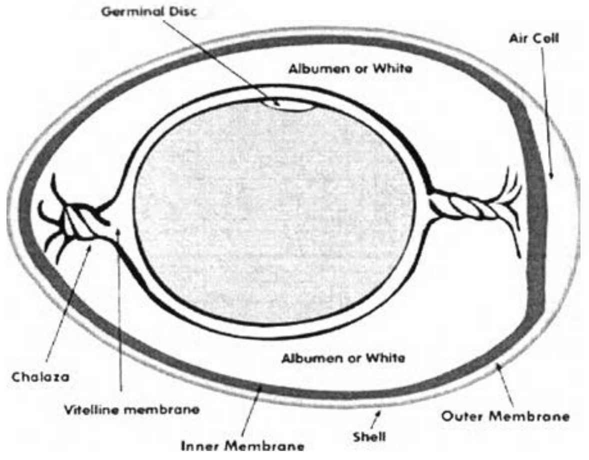


Figure 2.1 The structure of egg.
(http://www.sites.ext.vt.edu/virtualfarm/poultry/poultry_eggparts.html)

2.1.2 Structure of Eggshell

Eggshells are a function of protected impact force and microorganism, and acting gaseous permeability so a characteristic of eggshell is highly porous, approximately 6000–10000 pore per egg. (Bruce, *et al.*, 1994; Swanson, 2011) Chemical composition of eggshell consists of calcium carbonate (94% $CaCO_3$), calcium phosphate (1%), magnesium carbonate (1%), and organic substances (4%).

(Murakami, *et al.*, 2007) The eggshell is divided into three layers, as shown in Fig. 2.2. The first layer is a shell membrane (approximately 50 μm thick). Shell membrane's main function is to prevent micro-organism penetration and the membrane is made up of protein fibers

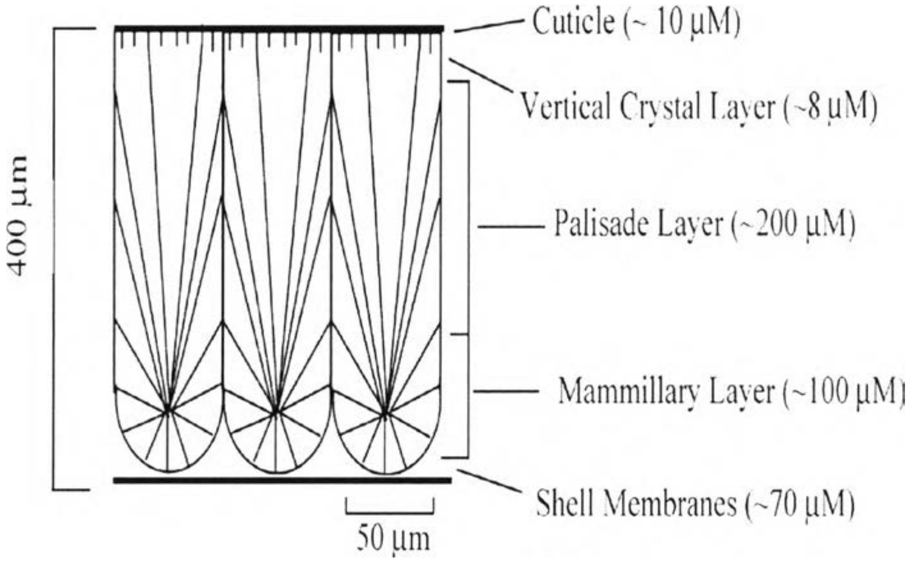


Figure 2.2 Schematic diagram of the structure eggshell. (Lammie, *et al.*, 2005)

The second layer can be sub-divided into three layers, consisting of the mammilla, palisade, and vertical crystal layers (approximately 300 μm thick). These layers consist of calcium carbonate crystals and are also constructed in such a manner that there are numerous circular openings, funnel-shaped holes called pore canals, on the surface of the shell. The third layer is cuticle which is the outer most layer of the eggshell (10 μm thick). The layer is largely an organic layer, containing protein as high as 90%. (Lammie, *et al.*, 2005; Tangboriboon, *et al.*, 2012)

Nowadays, eggshell is industrial residue that can contribute to pollution as it favors microbial action in the environment. (Eric, *et al.*, 1999) However, there are many methods to dispose eggshell, for example, to be used as fertilizer, animal-feed ingredient, discarded in municipal dumps, etc. (Daengprok, *et al.*, 2002; Macneil, 1997)

2.2 Hydroxyapatite

2.2.1 Introduction

Hydroxyapatite, calcium phosphate compound, has many types, depending on the ratio of Ca/P, as summarized in the Table 2.1. The ratio of the hydroxyapatite is 1.67 and also chemical formula is $Ca_{10}(PO_4)_6(OH)_2$. The crystalline structure of hydroxxyapatite is hexagonal form with unit cell parameters of a = b = 9.418 Å and c = 6.884 Å. Figure 2.3 shows the unit cell of the hydroxyapatite. (Aoki,1991)

Table 2.1 Calcium phosphate compound (Aoki, 1991)

Ca/P	สูตรเคมี	ชื่อ	ตัวย่อ
2.0	$Ca_4O(PO_4)_2$	Tetracalcium phosphate (Hilgenstockite)	TeCP (TTCP)
1.67	$Ca_{10}(PO_4)_6(OH)_2$ $Ca_{10\text{-}x}H_{2x}(PO_4)_6(OH)_2$	Hydroxyapatite Amorphous calcium phosphate	Hap ACP
1.50	$Ca_3(PO_4)_2$	Tricalcium phosphate (α, β. γ)	TCP
1.33	$Ca_8H_2(PO_4)_5.5H_2O$	Octacalcium phosphate	OCP
1.0	$CaHPO_4.2H_2O$	Dicalcium phosphate dehydrate (Brushite)	DCPD
1.0	$CaHPO_4$	Dicalcium phosphate (Monetite)	DCP
1.0	$Ca_2P_2O_7$	Calcium pyrophosphate (α, β, γ)	CPP
0.7	$Ca_7(P_5O_{16})_2$	Heptacalcium phosphate (Tromelite)	HCP
0.67	$Ca_4H_2P_6O_{20}$	Tetracalcium dihydrogen phosphate	TDHP
0.5	$Ca(H_2PO_4)_2.\ H_2O$	Monocalcium phosphate monohydrate	MCPM
0.5	$Ca(PO_3)_2$	Calcium metaphosphate (α, β, γ)	CMP

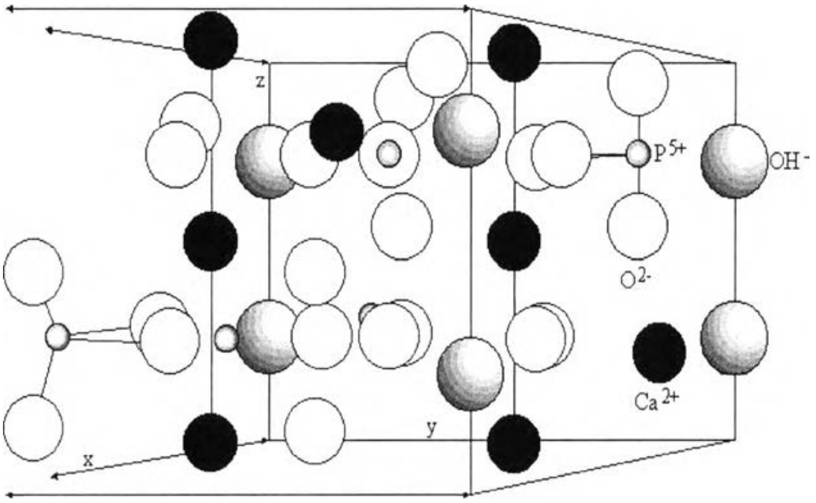


Figure 2.3 The unit cell of hydroxyapatite in a-axis.
(http://www.cuneyttas.com/biomim.htm)

Hydroxyapatite has long been used in medical applications, such as bone, dental etc., because it is bioceramic, biocompatible, bioactive, excellent thermally stable, and environmentally-friendly.

2.2.2 Methods of synthesized Hydroxyapatite

There are several methods for synthesizing hydroxyapatite, such as precipitation technique, sol-gel process, hydrothermal, multiple emulsion, biomimetic deposition, electrodeposition techniques etc. The precipitation technique and the sol-gel process are widely used for hydroxyapatite synthesis.

2.2.2.1 Precipitation Technique

This technique is to precipitate in aqueous solutions. Sometime it is called wet precipitation or chemical precipitation or aqueous precipitation. One aqueous solution containing calcium salt is mixed with phosphorus-containing solution and then both precursors undergo chemical reaction under a controlled pH, temperature, and pressure. Therefore, white precipitated powder is calcined at high temperature to hydroxyaptite structure. There are many routes for preparing hydroxyapatite via precipitation techniques, based on raw materials and conditions, as shown in equations (1-4) (Amit, 2010 and Dean-Mo, 2004).

$10\ Ca(OH)_2 + 6\ H_3PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$ ....(1)

$10\ Ca(OH)_2 + 6\ (NH_4)_2.HPO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H_2O + 12\ NH_4OH$ ...(2)

$7\ Ca(OH)_2 + 3\ Ca(H_2PO_4)_2.H2O \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 15\ H_2O$ ....(3)

$Ca(EDTA)^{2-} + HPO_4^{2-} + 2/5H_2O \longrightarrow 1/10Ca_{10}(PO_4)_6(OH)_2 + HEDTA^{3-} + 1/5\ OH^-$ ..(4)

2.2.2.2 Sol gel Process

The other technique that is a highly effective method for synthesizing hydroxyapatite is sol-gel process. This method provides a soft chemical route that not only improves the chemical and physical homogeneinity of the resulting product, but also gives high crystallinity and low impurities. Since there are many calcium and phosphorus raw materials that can be used to synthesize hydroxyapatite, therefore, many researchers studied on the conditions of the hydroxyapatite synthesis by various types of chemical substance, solvent, and temperature, as shown in the Table 2.2. (Dean-Mo, 2004)

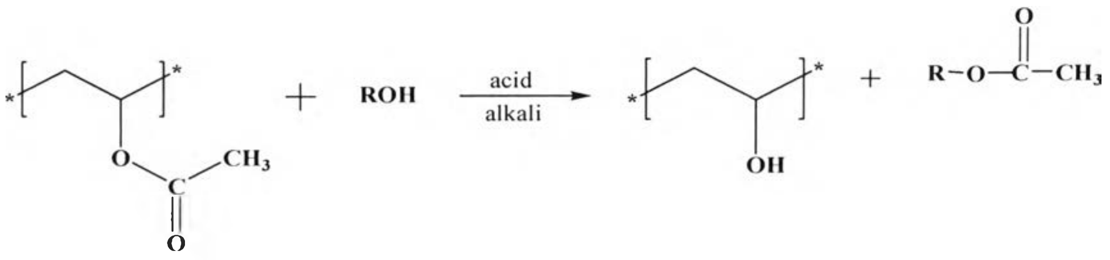
2.3 Polyvinyl alcohols

2.3.1 Introduction

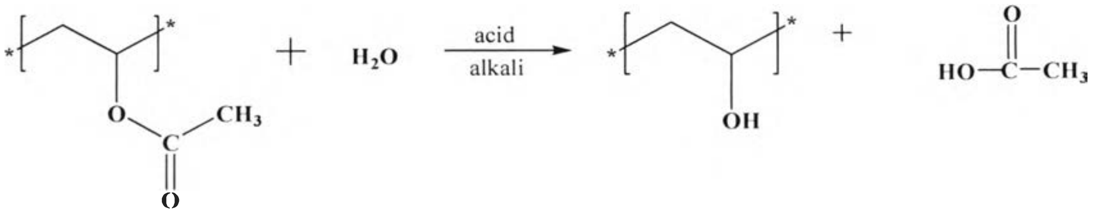
Polyvinyl alcohol cannot be synthesized by vinyl alcohol monomers due to the instability of monomer. However; polyvinyl alcohol can be prepared by transesterfication, hydrolysis, or aminolysis of polyvinyl acetate, as shown in Fig. 2.4. Polyvinyl alcohols can be fully hydrolyzed (97.5-99.5% degree of hydrolysis) and partially hydrolyzed (87-89% degree of hydrolysis). (Finch, 1992)

Table 2.2 Chemical precursors, mutual solvents, and the synthesis parameters required to form phase-pure crystalline hydroxyapatite in various sol-gel hydroxyapatites (Dean-Mo, 2004)

Chemical		**Solvent**	**Temperature**	**Time**	**Reference**
Calcium precursor	**Phosphorus precursor**				
$Ca(OC_2H_5)_2$	$PO(OC_2H_5)_3$	Ethanol	>450 °C	>24h	Y.Masuda,1900
$Ca(NO_3)_2$	$C_6H_5PCl_2$	Ethanol	>500 °C	-	T.Brendel,1992
$Ca(NO_3)_2$	$NH_4H_2PO_4$	Water	>500 °C	-	Q. Qiu, 1993
$Ca(NO_3)_2$	$HOOCCH_2PO(OH)_2$	Water	700 °C	-	H.Takahashi,1995
$Ca(OC_2H_5)_2$	$P(OC_3H_7)_3$	Ethanol	500 °C	24h	CS Chai,1995
$Ca(OC_2H_5)_2$	$PO(OC_2H_5)_3$	Ethanol	>600 °C	>24h	K.A. Gross,1998
$Ca(C_2H_3O_2)_2$	$PO(OC_2H_5)_3$	Water	>775 °C	>48h	Jilarenkatesa,1998
$Ca(C_2H_3O_2)_2$	$H_3PO_4/P_2O_5/P(OC_2H_3)_3$	Ethanol	>600 °C	-	D.B.,Haddow,1998
$Ca(NO_3)_2$	$C_4H_9(H_3PO_4)$	2-methyl-ethanol	300-500 °C	24h	C.M.Lopatin,1998
$Ca(NO_3)_2$	P_2O_5	Ethanol	500 °C	48h	W. Weng, 1998
$Ca(OC_2H_5)_2$	H_3PO_4	Methanol	>600 °C	24h	P. Layrolle, 1998
$Ca(NO_3)_2$	$PO(OC_2H_5)_3$	2-methyl-ethanol	600 °C	>16h	M.F.Hsieh, 2001



Hydrolysis:



Aminolysis:

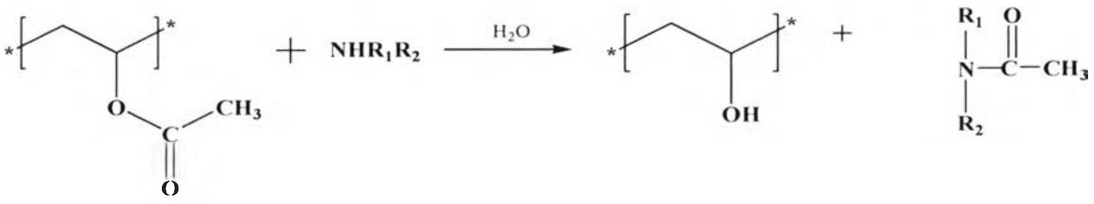


Figure 2.4 Transesterfication of polyvinyl acetate to polyvinyl alcohol.

2.3.2 Properties

Polyvinyl alcohol, a hydrophilic polymer soluble in water, has excellent chemical resistance, biodegradability, and physical properties. The properties depend on many factors, such as polyvinyl acetate starting material, degree of hydrolysis, molecular weight, water content, etc. Figure 2.5 shows properties of polyvinyl alcohol, depending on degree of hydrolysis of polyvinyl acetate and molecular weight. (Finch, 1992; Tang, *et al.*, 2011; Tao, *et al.*, 2003)

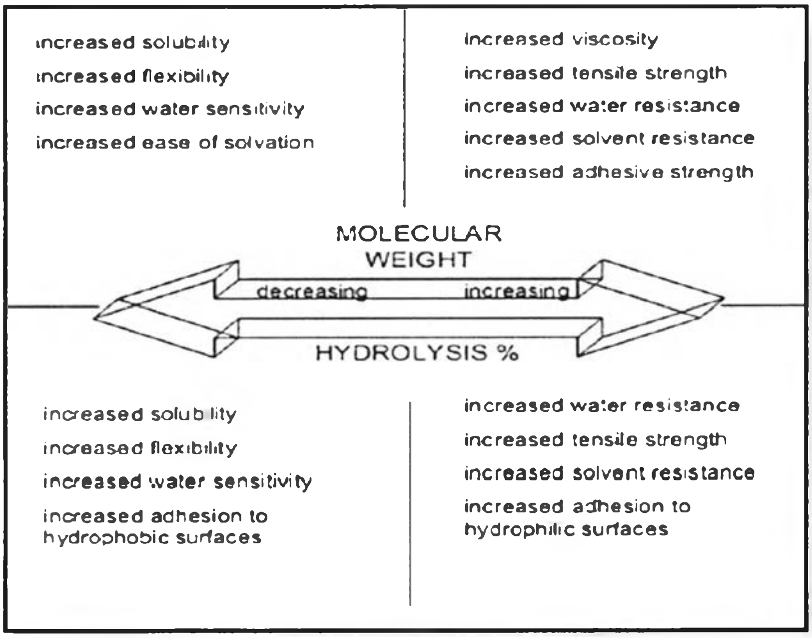


Figure 2.5 Effect of molecular weight and hydrolysis level on the physical properties of polyvinyl alcohol. (http://www.sekisui-sc.com/sekisui)

Generally, polyvinyl alcohol provides good hydrogen bonding and a high degree of crystallinity. Its melting point depends on the structure of the molecule. Atactics has the melting point in a range of 228° to 240 °C, isotactics 212° to 235 °C, and syndiotactics 230° to 267 °C. The glass transition temperatures are 85 ° and 58 °C for fully and partially hydrolyzed polyvinyl alcohol, respectively. The mechanical properties are a strong function of molecular weight and relative humidity. The tensile strength of PVA varies from 30 to 110 MPa, depending on the molecular weight and the relative humidity, as shown in Fig. 2.6. (Tao, 2003)

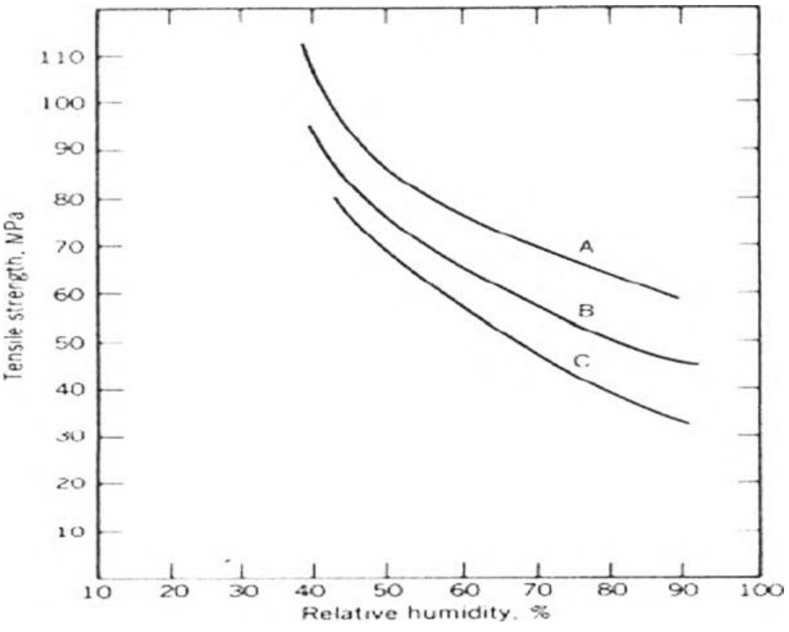


Figure 2.6 Tensile strength as a function of relative humidity for fully hydrolyzed poly(vinyl alcohol) films, having degree of polymerization of A) 2400; B) 1700; and C) 500. (Tao, 2003)

2.3.3 Applications

Polyvinyl alcohol is used in many applications, for example, textile wrap. Polyvinyl alcohol must have high mechanical properties due to high cohesive power during weaving, but low crystalline in order to dissolve to de-size after weaving. On surface sizing agent of paper coating, polyvinyl alcohol should have suitable viscosity for using in high-speed paper-make machine, high strength for enhancing paper strength, and high crystallinity for providing water resistance. Nowadays, polyvinyl alcohol is used in many biomedical applications because of its nontoxic, noncarcinogenic, biodegradable, and bioadhesive characteristics. Polyvinyl alcohol is approved for use in several medical applications, including artificial skin, controlled release drug delivery systems, contact lenses, wound dressings, cardiovascular devices, etc. (Bajoai, *et al.*, 2006; Finch, 1992)

2.4 Aerogels

2.4.1 Introduction

Aerogels are prepared via sol-gel process, followed by replacing wet gel with gas without collapsing gel network, as shown in Fig. 2.7. They are highly porous and specific surface area materials Physical properties and structure of the aerogels depend on precursors and the sol-gel process parameters, namely, type and concentration of precursor, type of solvent, type of catalyst, temperature, pH, time, and type of drying. (Aegerter, *et al.*, 2011; Hüsing, *et al.*, 1988)

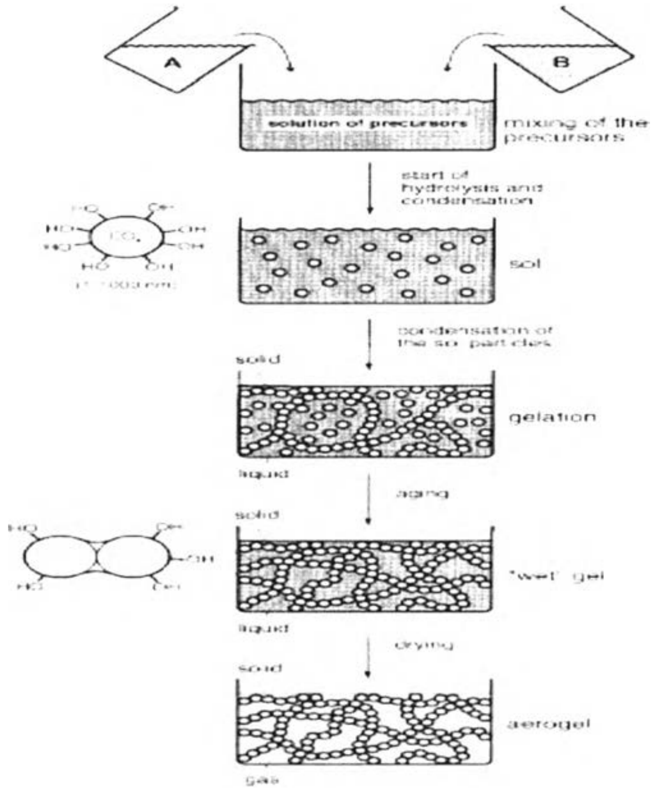


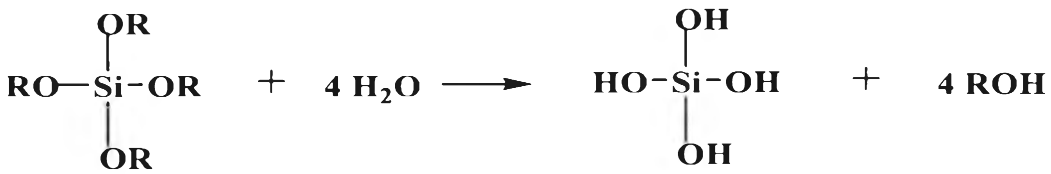
Figure 2.7 General scheme for preparing aerogels by sol - gel processing. (Hüsing, *et al.*, 1988)

2.4.2 Type of aerogel materials

2.4.2.1 Inorganic aerogels

All metals or semi-metal oxides are known to form gels, and served for the production of aerogels, such as alumina (Al_2O_3), titania (TiO_2), zirconia

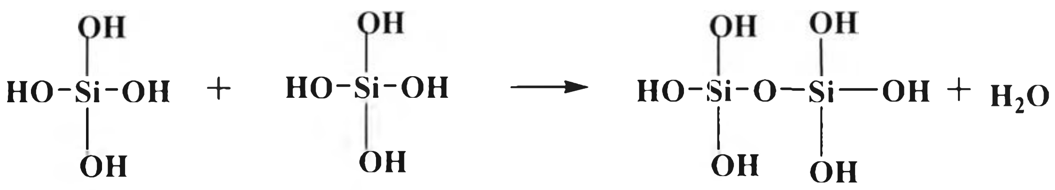
(ZrO_2), and silica (SiO_2) aerogel. Silica (SiO_2) aerogel is the most popular inorganic aerogels. (Hüsing, *et al.*, 1988) The synthesis of silica aerogel can be divided into 3 steps: The first step is gel preparation by sol-gel process. The second one is an aging step which gel prepared from the first step is aged in its mother solution. The last step is to dry the gel to remove liquid without collapsing the gel structure. The most common precursors for silica aerogel are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). Mechanism of silica aerogel consists of hydrolysis, condensation, and polymerization. The hydrolysis is first started by mixing precursor and water to generate hydroxyl group attaching to silicon atom, as shown in Fig. 2.8. (Alnaief, 2011; Dorcheh, *et al.*, 2008; Folgar, *et al.*, 2007)



$$RO-\overset{OR}{\underset{OR}{Si}}-OR + 4\,H_2O \longrightarrow HO-\overset{OH}{\underset{OH}{Si}}-OH + 4\,ROH$$

Figure 2.8 Hydrolysis reaction of alkoxysilane.

The second reaction, condensation, occurs when the silica hydroxyl groups interact with each other to produce siloxane bone, as shown in Fig. 2.9. (Folgar, *et al.*, 2007)



$$HO-\overset{OH}{\underset{OH}{Si}}-OH + HO-\overset{OH}{\underset{OH}{Si}}-OH \longrightarrow HO-\overset{OH}{\underset{OH}{Si}}-O-\overset{OH}{\underset{OH}{Si}}-OH + H_2O$$

Figure 2.9 Condensation reaction of alkoxysilane.

The last reaction is to polymerize or to continue the condensation to form a three-dimensional network, as shown in Fig. 2.10. (Folgar, *et al.*, 2007)

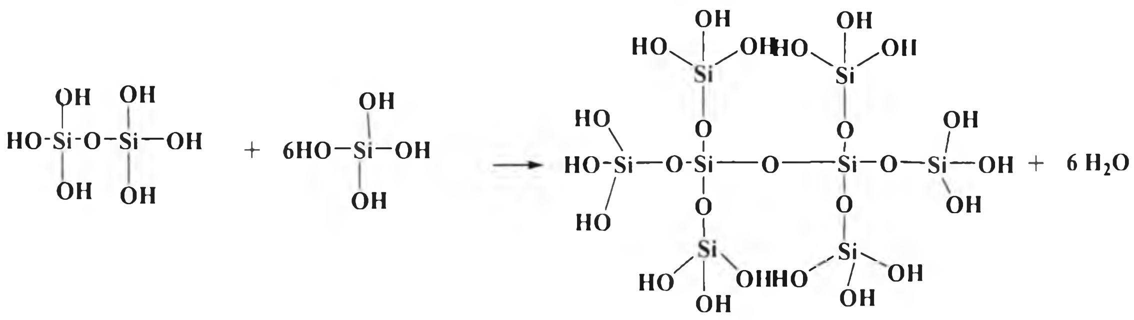


Figure 2.10 Polymerization reaction of alkoxysilane.

2.4.2.2 Organic aerogels

Organic aerogels are synthesized by polymerization of multifunctional organic monomers in dilute solution, followed by supercritical, freeze or ambient-pressure drying. Organic aerogels can be made from resorcinol formaldehyde, phenol formaldehyde, melamine formaldehyde, phenolic-furfural, cresol formaldehyde, polyimides, polystyrenes, polyurethanes, etc. The structure and properties of organic aerogels depend on precursor, solvent, catalyst concentration, and the pH of the solution. (Hüsing, *et al.*, 1988) Resorcinol formaldehyde aerogel is an important class of organic aerogel and categorized as a phenolic resin using phenol and formaldehyde as starting materials, as shown in Fig. 2.11. Synthesis of resorcinol formaldehyde aerogels is carried out by dissolving resorcinol in water and catalyst, followed by adding formaldehyde. The reaction occurs through hydroxymethylated resorcinol, the hydroxymethyl groups are then condensed with each other to form nanometer-sized clusters, becoming wet gel. After drying process, resorcinol formaldehyde aerogel is obtained. (Aegerter, *et al.*, 2011)

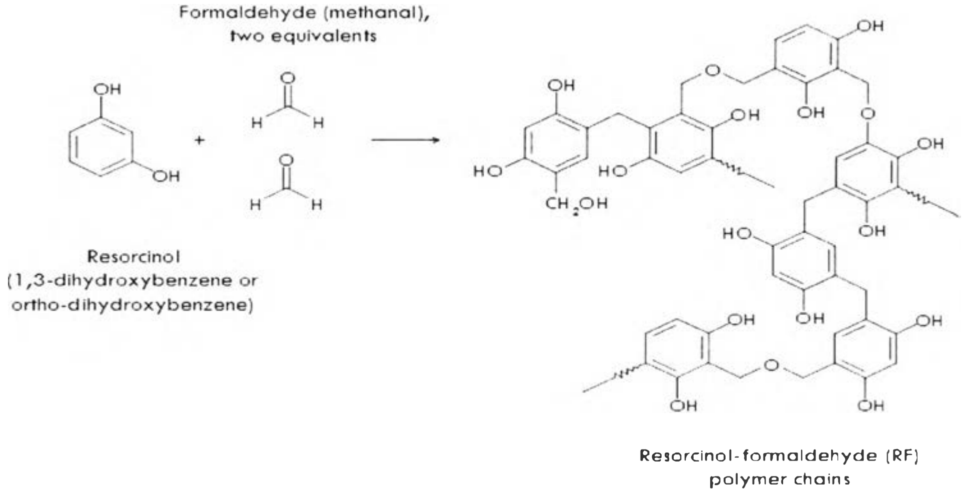


Figure 2.11 Polymerization of resorcinol and formaldehyde.
(http://www.aerogel.org)

2.4.2.3 Inorganic-organic hybrid aerogels

Inorganic-Organic hybrid aerogels are combined organic molecules with structural elements of inorganic materials. The advantages of these aerogels over inorganic areogel are highly hydrophobic and elastic properties. A general method is to combine organic molecules or groups during the sol gel processing. There are many types of inorganic-organic hybrid aerogels, as shown in Fig. 2.12. (Hüsing, *et al.*, 1988)

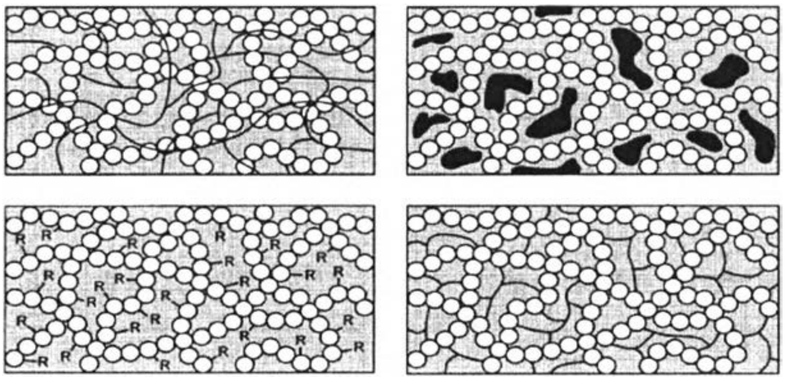


Figure 2.12 Inorganic- organic hybrid networks obtained by sol- gel processing.
(Hüsing, *et al.*, 1988)

From Fig. 2.12; top left figure shows interpenetrating networks in inorganic-organic hybrid aerogels, not connecting networks. For example, interpenetrating acrylamide-SiO_2 networks is an organic polymer generated in situ during the sol-gel reaction by radical polymerization of a vinyl monomer and TMOS undergone hydrolysis, condensation, and polymerization reaction to form a three-dimensional network, as shown in Fig. 2.13.

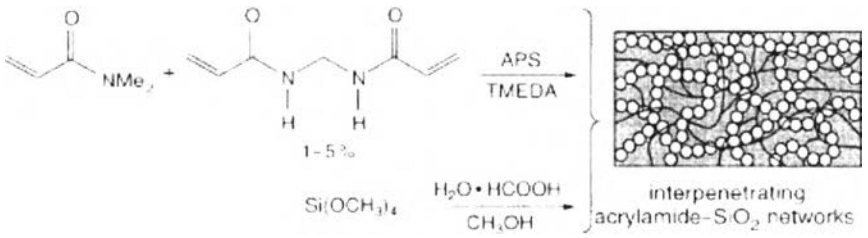


Figure 2.13 Formation of two interpenetrating networks (inorganic-organic) by simultaneous sol gel reaction and polymerization of N,N-dimethylacrylamide. (Hüsing, *et al.*, 1988)

For top right Fig. 2.12, inorganic-organic areogels are incorporation of organic molecules into inorganic aerogels. The organic molecules are embedded into gels without chemical bonding. This aerogel type is prepared by dissolving the organic molecules in the precursor solution to form gel matrix around and trap inorganic aerogels. However; the limitation of this type is that organic molecule is washed out during drying process, for example, incorporating a fluorescent dye into the gel network. (Hüsing, *et al.*, 1988)

For bottom right and left Fig. 2.12; inorganic-organic areogels are modification/functionalization of inorganic materials with organic substituents. The more important modifications of aerogels are based on covalent bonding of the organic groups, for example, modification of organic substituents on silane precursors, as shown in Fig. 2.14.

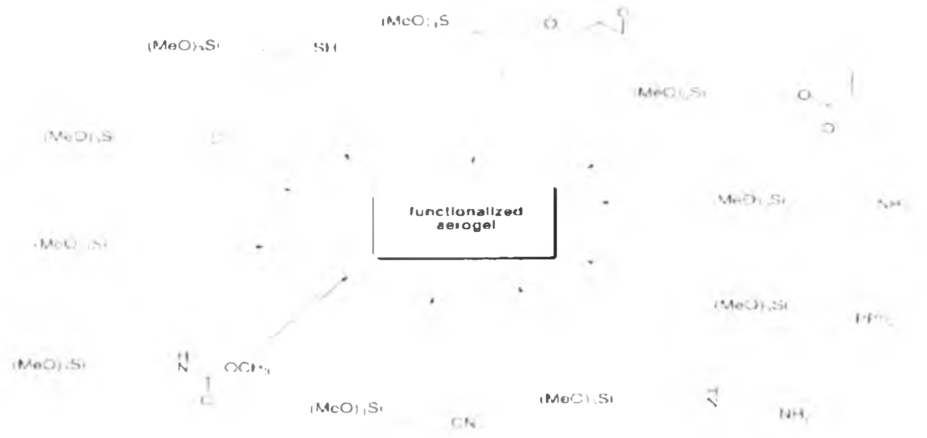


Figure 2.14 Silane precursors with organic substituents used for preparing functionalized aerogels. (Hüsing, *et al.*, 1988)

2.4.3 Drying method for aerogel

During the sol-gel process, the precursor changes from sol to gel. The sol formation is colloidal suspension of tiny particles or polymers suspended in a liquid whereas the gel formation is that the size of primary particles stops to grow in size, instead, it agglomerates with another primary particles, forming clusters of particle structure or three dimension networks. (Alnaief, 2011) However, the gel formation contains solvent, residues, unreacted precursors, and the by-product. Thus, they must be removed using drying method. Evaporation of the liquid from a wet gel is very complicated. For aerogels, drying methods of removing liquid form gel are necessary without collapsing the gel solid network. There are three types of the drying method for aerogels, namely, supercritical, ambient-pressure, and freeze drying methods. (Hüsing, *et al.*, 1988)

2.4.3.1 Supercritical Drying

In this method the solvent is put into the supercritical state, thus, there are no liquid/gas interfaces in the pores during drying and no pore structure collapse. Supercritical drying can be performed along pathway A or B, see Fig. 2.15.

For the pathway A, the temperature is slowly raised, resulting in an increase in pressure. The temperature and the pressure are adjusted to values above the critical point of the corresponding solvent (Tc, pc) and kept there for a certain period of time. The fluid is then slowly vented at constant temperature, resulting in a drop in pressure. The pathway B is different. Drying is often performed in a way that the vessel is prepressurized with nitrogen to avoid evaporation of the solvent.

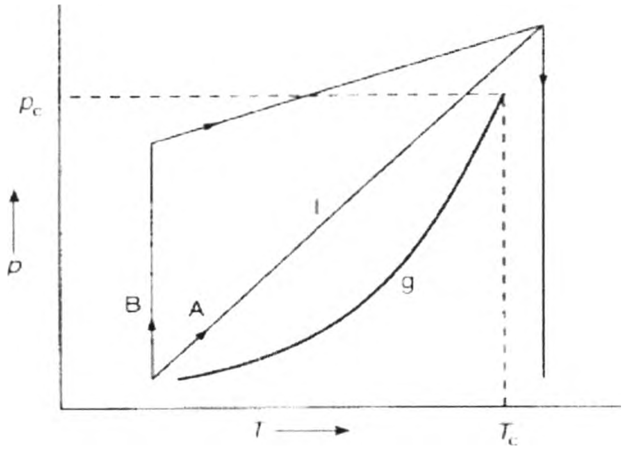


Figure 2.15 Schematic representation of the principle of supercritical drying. (Hüsing, *et al.*, 1988)

There are two general methods in the supercritical drying: high temperature supercritical drying (HTSCD) consisting of water, methanol, ethanol, and acetone, and low temperature supercritical drying (LTSCD) consisting of carbon dioxide, nitrous oxide, methane, ethane, and propane. Table 2.3 shows the critical conditions of some solvents. (Hüsing, *et al.*, 1988)

Table 2.3 Critical constants for some solvents

Solvent	**T_c [°C]**	**P_c [MPa]**	**V_c [cm^{-3}mol^{-1}]**
Methanol	240	7.9	118
Ethanol	243	6.3	167
Acetone	235	4.7	209
Water	374	22.1	56
Carbon dioxide	31	7.3	94

2.4.2.2 Ambient-Pressure Drying

The ambient-pressure drying is simple and less expensive method. This technique is drying at ambient conditions (subcritical drying) without collapsing the gel network because the contact angle between the pore liquid and the pore walls minimizes the capillary force by modification of the inner surface and variation of the solvent. (Hüsing, *et al.*, 1998)

2.4.2.3 Freeze-Drying

This method eliminates liquid/gas interface problem, causing collapsing of network. The freeze drying process is to freeze the pore liquid, followed by subliming under vacuum. The temperature is raised to allow the ice sublimed (Fig. 2.16b). The main problem with this technique is nucleation and growth of the solvent crystal that may destroy the network. However; this problem is dissolved by using low expansion coefficient of solvent, high sublimation pressure, and rapid freezing in liquid nitrogen. (Aegerter, *et al.*, 2011; Hüsing, *et al.*, 1998)

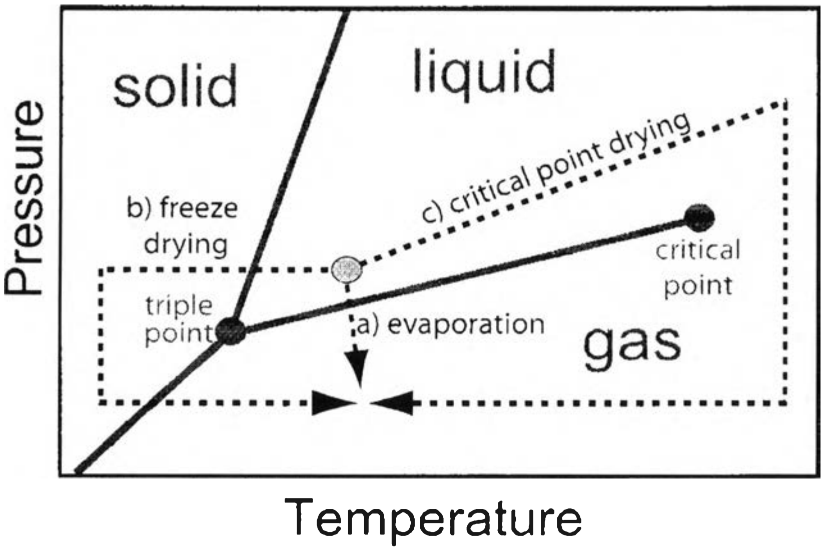


Figure 2.16 Principal of (a) supercritical dying and (b) freeze-drying. (Bryning, 2007)

2.4.4 Applications

Nowadays, aerogel technology plays an important role in the industry. Many researchers have studied the aerogel technology and there are continuously increasing publications about aerogel, as shown in Fig. 2.17.

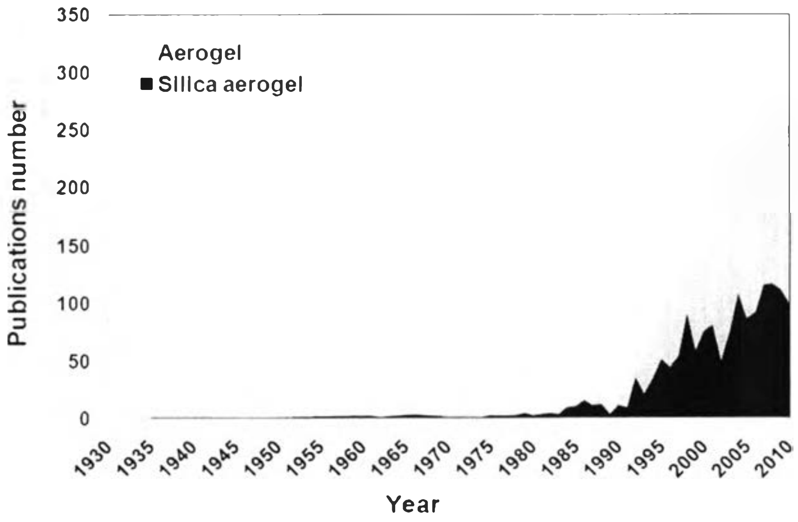


Figure 2.17 Publications number of aerogel. (Alnaief, 2011)

Based on specific properties, aerogels are used in many applications, and potential applications for aerogels are wide ranging and unlimited, as can be seen in Table 2.4. (Hrubesh, 1988)

2.5 Bone

2.5.1 Introduction

Bone is a natural composite material, consisting of mineral, matrix, and water with the composition of approximately 60, 30, and 10%, respectively, of the total weight of bone. The matrix component of the bone is organic matter (type I collagen) that highly aligned, yielding an anisotropic structure. The organic matter of bone is responsible for tensile strength. The mineral component, inorganic matter (calcium phosphate), of the bone gives rise to the compressive strength.

Table 2.4 Identifications of aerogel properties, features, and applications

Property	Features	Applications
Thermal conductivity	-best insulating solid -transparent -high temperature -light weight	-architectural and appliance insulation, portable cooler, transport vehicles,pipe,cryogenic,skylight -Space vehicles and probes,casting molds
Density and Porosity	-lightest synthetic solid -homogeneous -high specific surf. area -multiple compositions	-catalysts, sorbers, sensors, fuel storage, ion exchange -targets for ICF, X-ray lasers
Optical	-low refractive index solid -transparent - multiple compositions	-cherenkov detectors, lightweight optics, light guides, special effect optics
Acoustic	-lowest sound speed	-impedance matchers for transducers, range finders, speakers
Mechanical	-elastic -lightweight	-energy absorber, hypervelocity particle trap
Electrical	-lowest dielectric constant -high dielectric strength -high surface area	-dielectrics for ICs, spacers for vacuum electrodes, vacuum display spacers capacitors

Functions of bone are to protect soft tissue and produce red and white blood cells and minerals. There are two types of bone, compact or cortical, and spongy or trabecular bone (Fig. 2.18). The compact bone is the outer of bone which is smooth and dense. These characteristics affect to mechanical properties, giving a high compressive strength in the longitudinal direction, approximately 131–224 MPa, a high Young's modulus, approximately 17-20 GPa, and also exhibits good fracture toughness. The interior of the bone is spongy, which is highly porous, thus, the mechanical properties depend on density. Compressive strength of the spongy bone varies with the second power of density which has approximately value of 5–10 MPa, whereas Young's modulus scales as the second or the third power with values ranging from 50 to 100 MPa. (Mickiewicz, 2001)

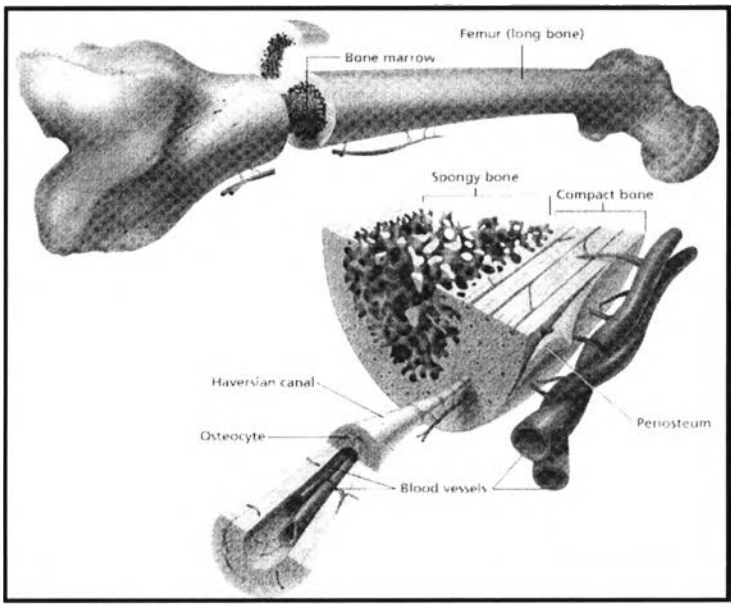


Figure 2.18 Structure of bone. (Nacharoen, 2009)

2.6 LITERATURE REVIEW

There are many researches relating to aerogels from eggshell for artificial bone project. Raw materials of this project are eggshell and polyvinyl alcohol for aerogel fabrication to be used as artificial bone.

Eggshell cannot be used directly for aerogel because it has many compositions in the eggshell. In 1999, Rivera *et al.* found that eggshells consist of organic and inorganic components. They studied two-stage thermal treatment of eggshell in order to prepare calcium oxide for biomedical material. The first stage was to heat the eggshells to 450 °C for 2 h. At this temperature, any organic residue is destroyed.

The second state was to heat the sample to 900 °C for 2 h at which $CaCO_3$ in the eggshells transforms into calcium oxide (CaO) by freeing carbon dioxide (CO_2). In 2005, Birol *et al.* studied the effect of temperature using X-ray diffraction (XRD), infrared (IR), and electron spinning resonance (ESR) spectra of chicken eggshell at the temperature range of 25–900 °C, and found that $CaCO_3$ decomposes at 900 °C for 1 h to give CaO and CO_2 products. In 2009, Tangboriboon *et al.* synthesized purify calcium oxide from eggshell by calcinations from 300 to 1000 °C for 1, 3, 5 h, and found that the best condition was to calcine at 900 °C for 1 h to obtain the pure fine grain of calcium oxide with white soft powder, 98%purity, hexagonal form, and ceramic yield of 65.92%, high porosity, good particles size distribution, and low dielectric constant.

Calcium oxide from eggshell has been used in many applications, for example, in 2009, Sanosh *et al.* studied on utilization of biowaste eggshells to synthesize nanocrystalline hydroxyapatite powders by simple sol–gel precipitation technique using CaO derived from chicken eggshells. The product was used in bone grafting application. In 2010, Tangboriboon *et al.* studied on synthesis of calcium zeolite type A catalysts as adsorbents used for air separation from eggshells. They prepared calcium oxide from eggshell by thermal treatment and then mixed with other chemicals using $CaO:Al_2O_3:Na_2O:SiO_2$ molar ratio of 1:1:2:8 by a sol–gel process and calcined at 300 °C for 1 h.

The other raw material is polyvinyl alcohol, a hydrophilic polymer and water soluble material. Polyvinyl alcohol has excellent chemical resistance, physical properties, and biodegradability. Hence, it has led to develop many commercial products, based on this polymer. In 2000, Hassan *et al.* studied structure and application of polyvinyl alcohol hydrogel, and focused on the area of medical and pharmaceutical applications. Generally, hydrogel is hydrophilic, crosslinked polymer which swells when placed in water. Polyvinyl alcohol can be changed from solution to hydrogel by chemical or physical crosslinking. Chemical crosslinking of polyvinyl alcohol needs difuncional crossliking agent, such as glutaraldehyde, acetaldehyde, formaldehyde, and other mono aldehydes. However, the crosslink agents are not acceptable for biomedical applications because toxic residue from the crosslink agent will result in undesirable effect. Other method of the chemical crosslinking is to use electron beam or γ-irradiation. These techniques have advantages over the use of chemical crosslink agent as they do not leave behind toxic and elutable agents, but cause bubble formation during process. The best condition of preparing hydrogel polyvinyl alcohol for biomedical application is physical crosslinking due to crystallite formation. This method is not toxic and also exhibits higher mechanical strength than other methods because the mechanical load can be distributed along the crystalline of three-dimension structure. The preparation of polyvinyl alcohol hydrogel is carried out by freezing and thawed technique. The properties of the obtained hydrogel depend on the molecular weight of polymer, the concentration of aqueous polyvinyl alcohol solution, the temperature and time of the freezing and thawed process, and the number of freezing/thawing cycle.

In this project, fabrication of aerogel using freeze-drying technique was carried out. This method is popular for aerogel fabrication because of simple and inexpensive technique. In 2006, Bandi and Schiraldi studied thermal behavior of clay aerolgel/polyvinyl alcohol using freeze–drying. Composites obtained had low density, and glass transition temperature (*Tg*) behaviors of clay/polyvinyl alcohol composites were higher than the matrix. However, thermal behaviors were a function of size, loading, and dispersion of the clay and clay aerogel in the polymer matrix. Polyvinyl alcohol is suitable to be used in biomedical application because of nontoxic, noncarcinogenic, biodegradable, and bioadhesive characteristics. Thus, many researchers used polyvinyl alcohol to study for biomedical application. In 2008, Wu *et al.* studied behaviors of hydroxyapatite reinforced polyvinyl alcohol hydrogel composite for artificial cartilage, and found that the bioactivity and mechanical properties of the composite depended on the hydroxyapatite content in the composite. In 2009, Zhang *et al.* studied the friction and wear mechanism of polyvinyl alcohol/hydroxylapatite composite hydrogel using freezing and thawing. The results showed that polyvinyl alcohol/hydroxylapatite composite hydrogel had the cross-link network microstructure which is bone-like structure, and the physical properties of the composite depend on the freezing-thawing cycle and hydroxyapatite content.

In 2006, Neumann *et al* reviewed composite of calcium phosphate and polymers as bone substitution material. Preparation of this composite as artificial bones must concern about mechanical properties, biocompatibility, processing/shaping, and compensation of acidity. In 2007, Wang *et al.* synthesized and characterized collagen-chitosan-hydroxyapatite artificial bone matrix. They prepared artificial bone matrix through solid-liquid phase separation method. The products had three dimension porous structure and gave good biocompatibility, but rupture strength and rupture elongation of this composite were less than collagen matrix. In 2009, Tao *et al* prepared icariin and chitosan/hydroxyapatite using freeze-drying technique for bone tissue engineering. The results of product showed that icariin did not affect physical structure of composite, but decreased mechanical properties of composite. In 2010, Zhi *et al.* applied the biocomposite of calcium phosphate cement (CPC)/polylactic acid-polyglycolic acid (PLGA) into animal for bone defect reparing. The composite was good mechanical, three-dimension porous, and able to promote growth of bone tissue and accelerate repairing of bone defect. In 2012, Kane *et al.* studied the effects of the hydroxyapatite reinforcement weight fraction and morphology on the architecture and compressive mechanical properties by using freeze-dried collagen scaffolds for bone graft application. The results showed high porous structure, containing 90–96% porosity, which decreased with increasing hydroxyapatite content, and high compressive modulus, which increased with hydroxyapatite content.