



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogels: Structure and Preparations

Hydrogels are three dimensional hydrophilic polymer networks and swell in water or in biological fluids resulting in retaining a large amount of fluids in the swollen state. Water absorption in hydrogels are caused by hydrophilic functional group such as $-OH$, $-COOH$, $-CONH_2$ and $-SO_3H$ (Bouwstra et al., 1993). Water content in the hydrogels affect different properties, such as permeability, mechanical properties, surface properties and biocompatibility. Hydrogels show similar physical properties as living tissue in terms of the high water content, soft and rubbery consistency, and low interfacial tension with water or biological fluids (Blanco et al., 1996). Hydrogels can be classified into 4 types as pH sensitive, temperature sensitive, enzyme sensitive, and electrical sensitive (Kost et al., 2001).

Hydrogel Preparation

Hydrogels can be prepared by several techniques since they were proposed by Wichterle and Lim in 1960 (Wichterle et al., 1960).

- Solution polymerization crosslinking: In solution, monomers are mixed with the multifunctional crosslinking agent. The polymerization is initiated by thermal, UV-light, or by redox initiator system. The presence of solvent serves as heat sink, and minimizes temperature control problems. The crude hydrogels obtained need to be washed to remove the unreacted monomers, crosslinking agent, and the initiator before use (Wichterle et al., 1960).
- Suspension polymerization: This method is employed to prepare spherical hydrogel microparticles in the range of $1\ \mu\text{m}$ to $1\ \text{mm}$. In suspension polymerization, the monomer solution is dispersed in the non-solvent forming fine droplets, which are stabilized by adding the stabilizer. The polymerization is initiated by thermal decomposition of free radicals.

The prepared microparticles then washed to remove unreacted monomers, crosslinking agent, and initiator before use (Wichterle et al., 1960).

- Polymerization by irradiation: High energy radiation such as gamma and electron beam, have been used to prepare the hydrogels of unsaturated compounds. The irradiation of aqueous polymer solution results in the formation of radicals on the polymer chains. Also, radiolysis of water molecules results in the formation hydroxyl radicals, which also attack the polymer chains, resulting in the formation of macroradicals. Recombination of the macroradicals on different chains results in the formation of covalent bonds, and finally a crosslinked structure is formed. During radiation, polymerization macroradicals can interact with oxygen, and as a result, radiation is performed in an inert atmosphere using nitrogen or argon gas. The major advantage over chemical initiation is the production of relatively pure, residue-free hydrogels (Wichterle et al., 1960).
- Chemically crosslinked hydrogels: Polymers containing functional groups like $-OH$, $-COOH$, $-NH_2$, are soluble in water. The presence of these functional groups on the polymer chain can be used to prepare hydrogels by forming covalent linkages between the polymer chains. The crosslinking agents react with the functional groups present on the polymer, via addition reaction. These crosslinking agents, glutaraldehyde for an example, are highly toxic, and hence unreacted agents have to be extracted (Wichterle et al., 1960).
- Physically crosslinked hydrogels: Most of the chemical organic molecules to provide covalent crosslinking are toxic. An alternative way to form hydrogels is to apply the reversible ionic crosslinking or interpolymer complexes. In contrast to covalent crosslinking, no auxiliary

molecules such as catalysts are required (Ohkura et al., 1992). Chitosan is also known to form polyelectrolyte complex with poly(acrylic acid). The polyelectrolyte complex undergoes slow erosion, which gives a more biodegradable material than covalently crosslinked hydrogels (Kanaya et al., 1994 and Kanaya et al., 1995). Moreover, for some polymers, particularly poly(vinly alcohol) (PVA), hydrogel can be prepared by freezing and thawing of aqueous solution (Hassan et al., 2000).

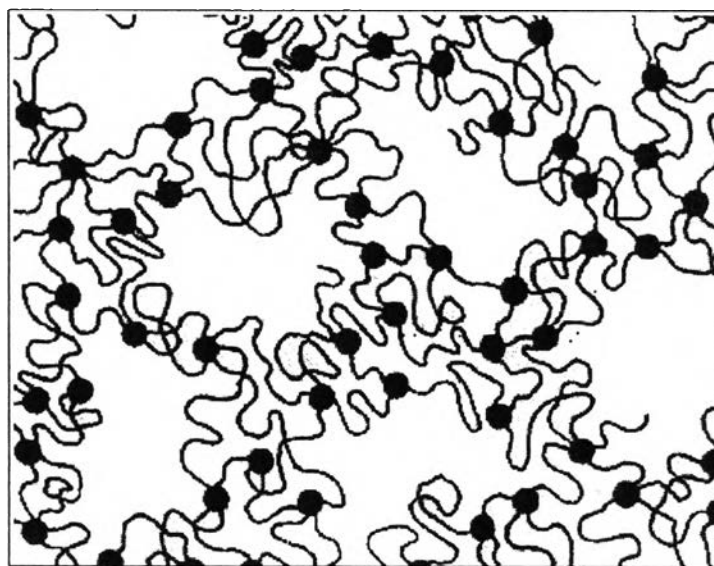


Figure 2.1 Schematic representation of structural model for PVA hydrogel prepared by repeated freezing and thawing. Solid circles represent PVA crystallites (Yokoyama et al., 1986).

Freezing-thawing Technique

The preparation of pure PVA hydrogels using the freezing and thawing technique was first reported by Peppas (1975). Aqueous solutions with PVA concentration varying from 2.5 to 15 wt% were frozen at -20°C . The thawing back to room temperature resulting in the formation of crystallites. Factors related to crystal formation are concentration of PVA in solution, freezing time, and thawing time. Structural model for the highly elastic PVA hydrogel which is prepared by the freezing and thawing can be postulated as shown in Figure 2.1. As shown in the model,

the hydrogel is composed of the following three kinds of phases: water phases or solution phases with a very low concentration of PVA, which in the frozen gel correspond to the crystal phases of ice; amorphous phases, in which every PVA chain is associated with water; PVA crystal phases, which restrain gross mobility of the amorphous chains (Yokoyama et al., 1986).

2.2 Introduction to Aerogels

Aerogels are materials which have numerous and fascinating properties over any solid ever tested such as lowest thermal conductivity, refractive index, sound velocity and dielectric constant. Aerogels gained a lot of interesting from scientists since it was first prepared in 1930's. Kistler proposed that a gel which composed of solid and liquid phase which was independent of each other. If the liquid phase was removed from the gel in non-destructive manner, a solid porous material would be left with approximately the same shape and volume as the original gel. For today's research has focused on potential application and more economic product routes (Fricke et al., 1997).

In the first step of aerogels synthesizing, these materials are prepared by low-temperature traditional sol-gel chemistry. However, in the final step most wet gels are often dried to remove liquid by several methods to obtain the hollow, porous skeleton. Different drying processes produced different name of the gel. The sol-gel and drying flowchart are shown in Figure 2.2 (Pierre et al., 2002).

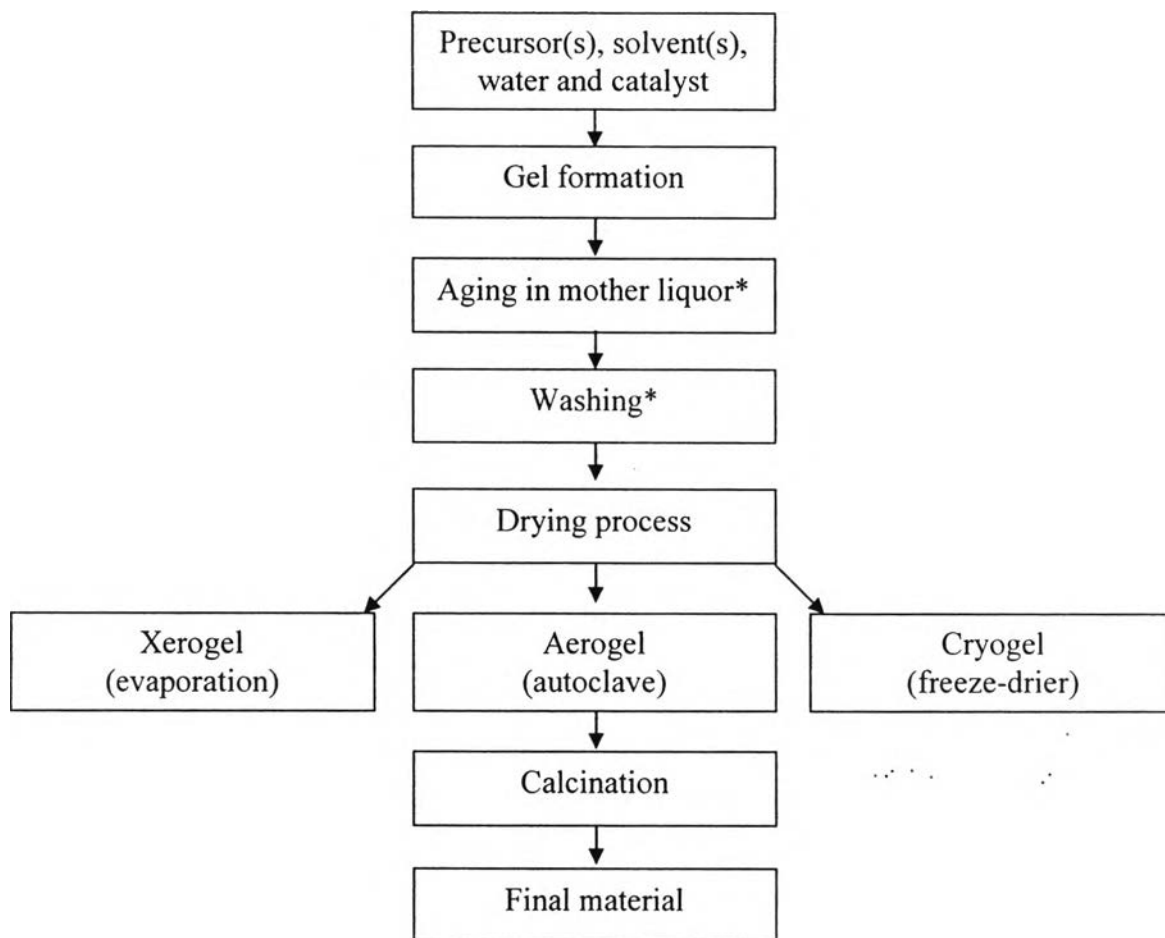


Figure 2.2 Sol-gel drying flowchart.

(*) The aging and washing steps are optional (Pierre et al., 2002).

Type of aerogels

There are 4 types of aerogels based on their chemical compositions:

- a) Metal oxide or inorganic aerogels
- b) Organic aerogels
- c) Carbon aerogels
- d) Clay aerogels

a) Metal Oxide or Inorganic Aerogels

This type of aerogel is obtained from condensation of the sol particles then the gel is formed in wet state. When the gel is dried up the aerogel will be obtained as shown in Figure 2.3.

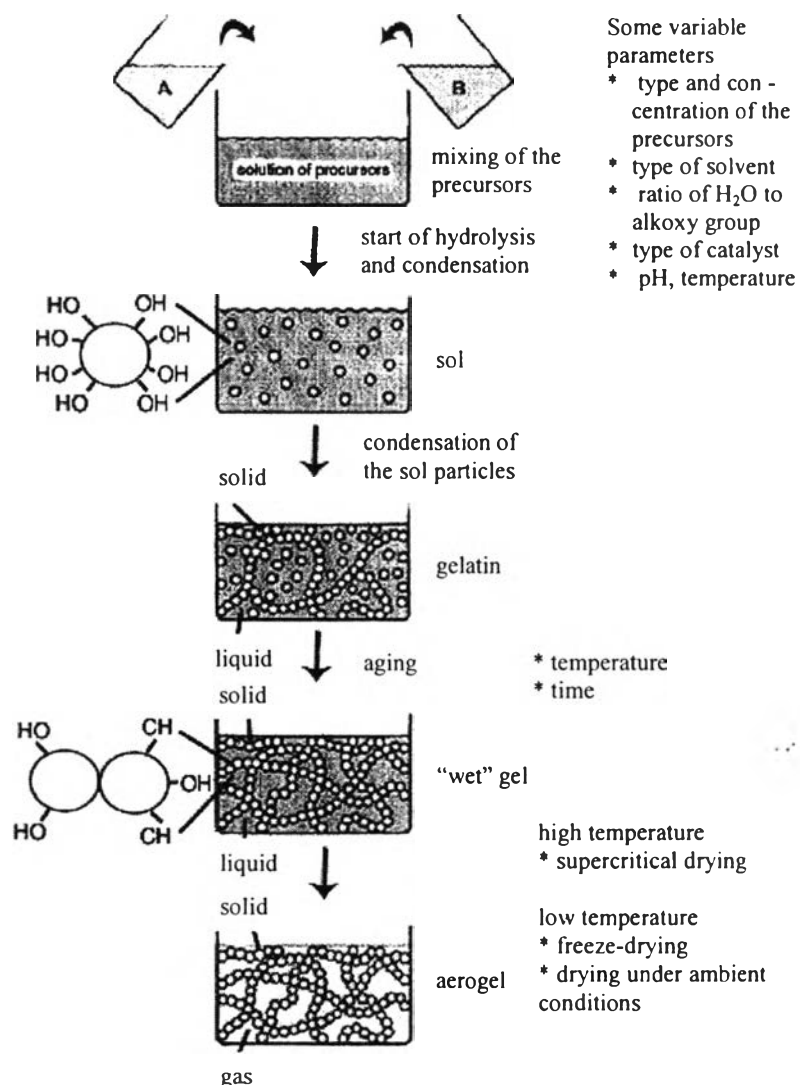


Figure 2.3 General scheme for preparing aerogels by sol-gel processing and some typical variable parameters (Schubert et al., 1998).

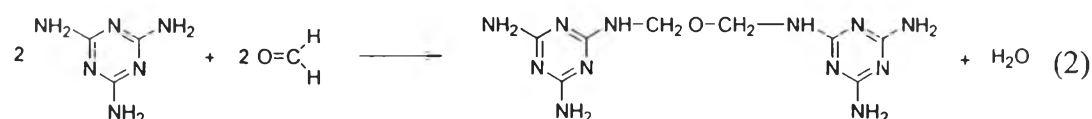
Silica aerogel is the first inorganic aerogel accidentally synthesized by Kistler in 1931 via Equation (1) (Kistler, 1932).



b) Organic Aerogels

For organic aerogels, they can be obtained from organic precursors. The organic precursors make organic polymers with strong -C-C- covalent bond. The most

extensively studies of organic aerogels are the resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF) aerogels. Polycondensation of resorcinol or melamine with formaldehyde is used to prepare this type of aerogel. The reactions are usually in slightly basic aqueous solution, often with sodium hydroxide or sodium hydrogen carbonate as gelation catalysts. The reaction for melamine is shown in Equation (2) (Pekala, 1998(a) and Tamon et al., 2000).



c) Carbon Aerogels

Most of carbon aerogels are obtained from pyrolysis of organic aerogels at temperature above 500°C (Tamon et al., 2000). The organic aerogels transform to an electrical conductive carbon network with some shrinkage. The porosity is depended on pyrolysis temperature. At pyrolysis temperature below 1000°C, large amount of microporosity is generated (Bock et al., 1998 and Petricevic et al., 1998). But when the pyrolysis temperature goes up to 2100°C, all micropores are almost disappeared (Reichenauer et al., 1998).

d) Clay Aerogels

Unlike the previous mentioned about type of aerogels, clay-aerogels do not need to follow the chemical condensation routes as described above. Clay-aerogels are formed by physical/electrostatic interaction between clay particles (Bandi, 2006). The conversion process of clay powder to clay aerogel was recently reported by Somlai in 2006. Clay aerogel was produced by blending clay and deionized water then suddenly freezing at -80°C and freeze-drying subsequently. After freeze-drying the clay gels, the robust, easily handled, sheet-like and highly ordered structure is obtained and stable gels were formed by using minimum concentration of 2 wt% of clay suspension (Somlai et al., 2006). The aerogel micrograph is shown in Figure 2.4.

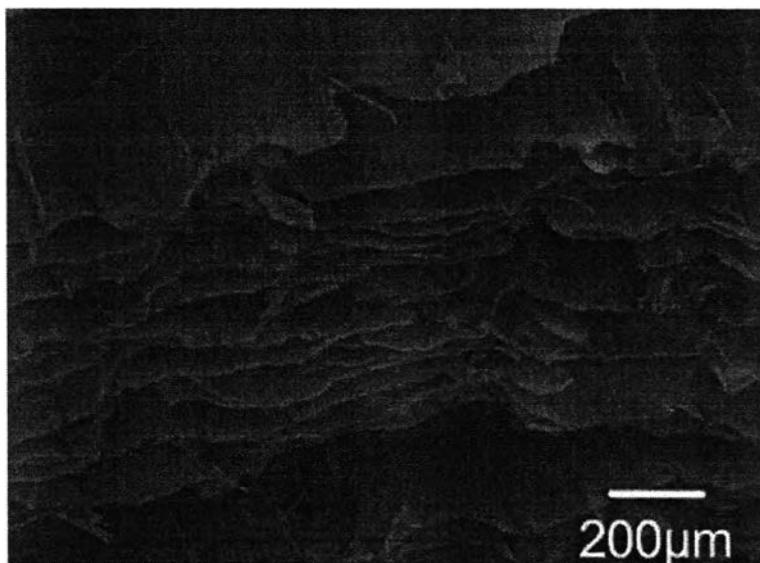


Figure 2.4 SEM image of freeze dried clay (Somlai et al., 2006).

2.3 Interpolymer Complexes (IPC)

Interpolymer complex is a complex of at least two different polymers or oppositely charged polymers. Interpolymer complexation between water-soluble polymers by hydrogen bonding has received much attention since 1959, when Smith et al. (1959) and then later Bailey et al. (1964) reported the complexation between poly(carboxylic acids), served as a common proton-donating components, and poly(ethylene oxide) (PEO) as for a proton-accepting parts. They demonstrated that the interaction between these polymers is driven by hydrogen bonding and the IPC stoichiometry approaches 1:1. While at low pH ($\text{pH} < 3.8$), the interaction results in phase separation; at higher pH, the polycomplex exists in solution. In the neutral pH region, they also observed some interaction between the two polymers.

A complexation between some certain polymers such as poly(carboxylic acids) and non-ionic polymers has hydrogen bonding as a major driving force for interpolymer interaction. Although the energy of a single hydrogen bond is comparatively low but when there is a simultaneous formation of a large number of intermolecular hydrogen bonds between two macromolecules, the strength of the interaction is very significant. The cooperativeness of the interaction provides a sufficiently stable ladder-type structure of IPC in comparison with small molecules, which associate via

single hydrogen bonds. In most cases, these ladder-type structures begin compacting immediately after their formation in order to reduce the surface contact with solvent molecules and the compact IPC particles continue to aggregate further as shown in Figure 2.5 (Khutoryanskiy et al., 2007).

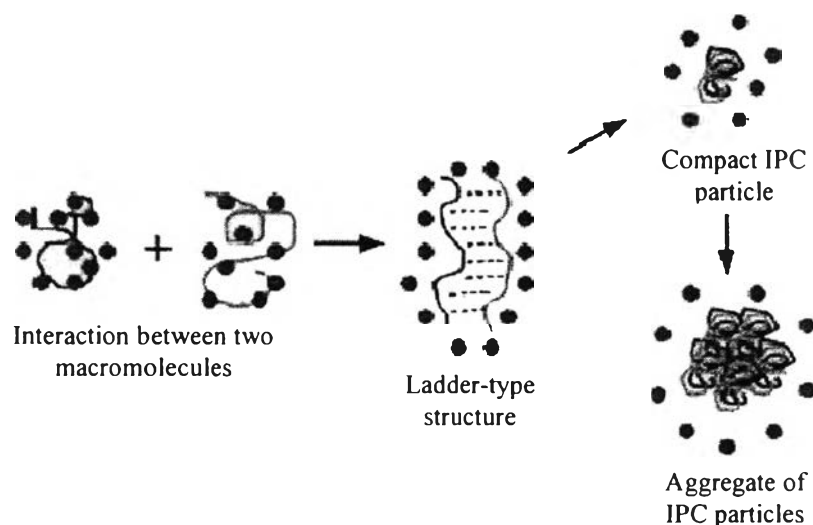


Figure 2.5 Scheme of IPC formation (circles are molecules of solvent).

Interpolymer complexes are found to be prepared by various type of polymers. PVA/PAA interpenetrating network films were prepared by polymerization of acrylic acid monomer in PVA solution. The solution obtained was then casted on glass plates and subjected to a freezing-thawing cycle. Subsequent washing and drying at room temperature gave the films. The DSC and ^{13}C CP/MAS NMR results showed the compatibility of PVA/PAA complex at low PVA concentration (less than 30% PVA composition) but phase separation occurred at high PVA concentration (Hernandez et al., 2005).

Paranhos (2007) studied the crystallinity of poly(vinyl alcohol)/sulfonated polyester (PVA/PES) hydrogels produced by freezing and thawing technique. The degrees of crystallinity of PVA/PES hydrogels from differential scanning calorimetry (DSC) are lower than pure PVA and glass transition temperature (T_g) is found to be decreased. This is due to interactions between PVA and PES. This leads to an increase on the amorphous content of the hydrogels.

Various types of hydrogen bonding structures (independence of N) of poly(acrylamide)/poly(vinyl alcohol) (PAM/PVA) IPC were purposed in Figure 2.6 by Demchenko (2001). PVA and PAM solutions were blended at 50/50 ratio then freeze-drying to prevent polymer chain movement. The WAXS patterns showed that PVA in PVA/PAM complex completely loses ability to crystallize. A new glass transition temperature from DSC indicates the compatibility of the IPC formation in polymer mixture.

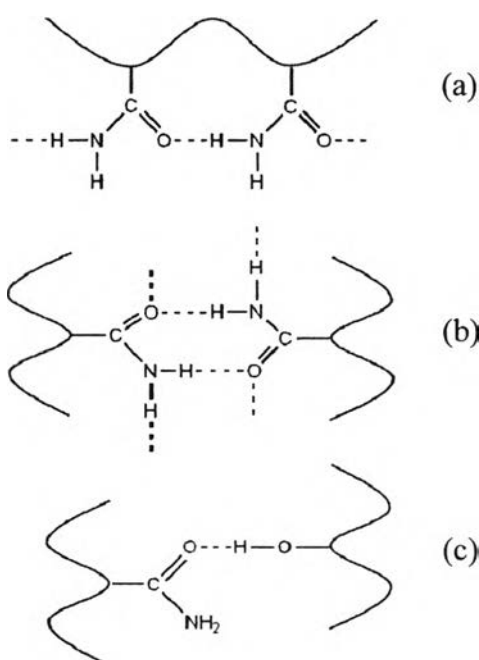


Figure 2.6 Hydrogen bonding structures of PVA/PAM ICP. (a) trans-multimers of amide groups of PAM, (b) cis-trans-multimers of amide groups of PAM, and (c) hydrogen bonds between chains (Demchenko, 2001).

Intermolecular interactions in blends of PVA with PAA were studied by Daniliuc in 1992. The miscibility of polymers is promoted by interactions such as ion-ion, dipole-dipole, ion-dipole, donor-acceptor and hydrogen bonding interactions. FTIR has been raised to prove the hydrogen bonding interaction forming between PVA and PVA. The analysis of the OH and C=O stretching region showed a rapid decrease of the crystallinity of PVA when the PAA content increases and its complete suppression when the PVA content equal or exceed 50 wt%. The OH absorp-

tion band shifts to higher frequency indicating weaker H-bonds in the blend than in the individual components.

2.4 Scope of the Present Work

The present work focuses on making PVA/PAA aerogel from interpolymer complexation of hydrogel. To avoid using toxic crosslinking agent, freezing-thawing technique is used to prepare physically crosslinked hydrogel. Freeze-drying in the next step gives aerogel. The heat treatment and the PVA content are also considered to enhance aerogel performances.