

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

1. Koh-samed's sand

Coral reefs are the largest shore structures occurred by plants and animals (Hopley, 2005), and also the most diverse of marine ecosystems (Pandolfli *et al.*, 2003). Although coral reefs are commonly associated with tropical shores, coral reefs are almost formed into a carbonate production and dominant siliciclastic sediment composition has been identified (Yamano *et al.*, 2001). The distribution of reef shores is limited by thermal considerations, water circulation, nutrient status and turbidity, and a thorough review of these factors is given in Woodroffe (2003).

Koh-samed's sand is a limestone which occurred from the shells of dead marine organisms such as clams, oysters, crayfishes, brachiopods, bryozoans, crinoids and corals, then live on the bottom of the sea. After that, their shells accumulate into piles and forming beds as limestone which is an important environments where early marine cementation, mainly by high-magnesian calcite and aragonite. Some limestone is pure calcium carbonate, but most is actually contained with other minerals from the sea bed, such as silicone dioxide (sand), iron oxides and silt, for Koh-samed's sand is not a pure calcium carbonate (Molenaar *et al.*, 1993).

2. Polyvinyl alcohol

2.1 Introduction of polyvinyl alcohol

Polyvinyl Alcohol (PVA) is an environmental friendly and water soluble synthetic polymer which is manufactured by polymerization of vinyl acetate monomer. Since the properties on which technical application of PVA depend are primarily its molecular weight and degree of hydrolysis.

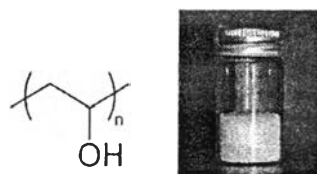
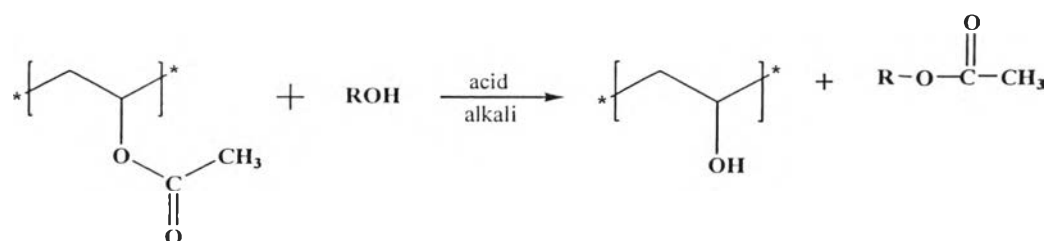
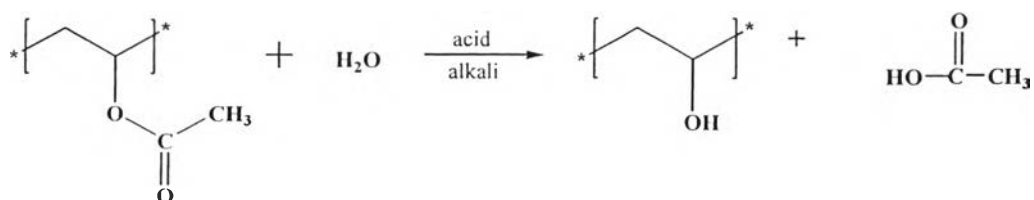


Figure 2.1 The chemical structure and the appearance of PVA.



Hydrolysis:



Aminolysis:

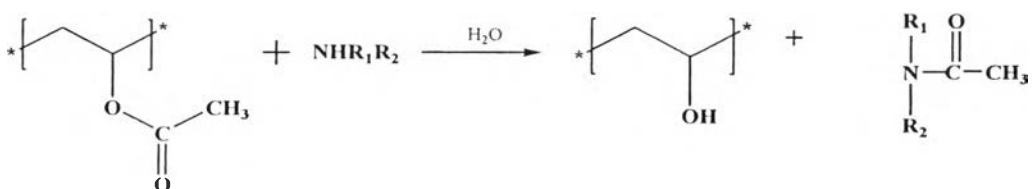


Figure 2.2 Transesterification of polyvinyl acetate to polyvinyl alcohol.

2.2 Properties of polyvinyl alcohol

Polyvinyl Alcohol is high polymer with excellent characters to dissolve easily in water but not to dissolve in common organic solvent and organic acids, with excellent film-forming property, oil resistant and chemical-resistant. It can react with formaldehydes to form polyvinyl acetal. Hydrogels from polyvinyl alcohol are water-swollen with crosslinked polymer networks, which often exhibit characteristics, such as tissue-like elasticity and mechanical strength and the appearance and feel of PVA hydrogel are similar to those of native arterial tissue (Nuttelman *et al.*, 2001).

2.3 Application of polyvinyl alcohol

Due to its unique features of high cohesiveness, membrane tenacity, smoothness, solvent resistance, gas inhibitor, wear resistance, protective colloid, and waterproof after specially treated, polyvinyl alcohol is widely applied in textile, building, papermaking, packing, timber processing, agriculture, printing, etc.

It has been extensively used in adhesive, in textile warp sizing and finishing, in paper size and coating, in the manufacturing of PVA emulsion, in the suspension polymerization of PVC, and as binder for ceramics, foundry cores and several of pigment. It is a hydrophilic, biodegradable and biocompatible synthetic polymer, which has been widely used in different areas of the biomedical field (Paradossi *et al.*, 2003).

3. The production of porous polymer particles

Filip *et al* (2012) studied about porous polymer particles, especially the ones that are spherical in shape, have been utilized in numerous applications for decades. They have been classified as macro-, meso- and microporous depending on the size of the pores, respectively >50 nm, $50\text{--}2$ nm and <2 nm. Two main features, their porous nature and higher crosslinking degree, differentiate them from gel-type polymer particles. These differences give raise to different characteristics such as high surface area, ability to uptake various solvents with different polarity and increased brittleness. Size, size dispersity, chemical nature and functionality can be mentioned as the other features that porous particles share with their nonporous counterparts, the gel-type particles. The variety of applications requires different combinations of the mentioned features.

4. Organic/Inorganic hybrid composite

Hybrid materials are composites consisting of two constituents at the nanometer or molecular level. Commonly one of these compounds is inorganic and the other one organic in nature. Thus, they differ from traditional composites where the constituents are at the macroscopic. Mixing at the microscopic scale leads to a more homogeneous material that either shows characteristics in between the two original phases or even new properties (Czegegy *et al.*, 2000). The hybridization effect has successfully increased the resistance of the hybrid composite to severe environmental degradation to the extent that it protects the internal structure of the composite from environmental damage, even though the surface of the composite gets severely degraded (Leong *et al.*, 2003).

Many natural materials consist of inorganic and organic building blocks distributed on the nanoscale. In most cases the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks or the soft tissue. Typical examples of such materials are bone, or nacre. The first hybrid materials were the paints made from inorganic and organic components that were used thousands of years ago.

The sol-gel process developed in the 1930s was one of the major driving forces what has become the broad field of inorganic-organic hybrid materials. In 2003, Leong *et al* has been done to determine the mechanical and thermal properties of single-filler and hybrid-filler PP composites, which have generated very interesting results that demonstrate the effectiveness of hybrid fillers in enhancing the properties of PP. The treatment of fillers with surfactants on material explored the more efficacy of hybrid composite. In 2004, they found that talc and calcium carbonate (CaCO_3) which filled in PP influent effect to the natural weathering on the mechanical and morphological properties as well as melting and crystallization. The crystallization and melting behavior of degraded polymer was studied by differential scanning calorimeter (DSC) while the exposed surface morphology of the samples was studied under scanning electron microscope (SEM). Mechanical testing such as tensile, flexural and impact tests were also done to determine the physical aspects of the composites.

It is worthy to note that the hybrid-filler composites have fared extremely well in weathering conditions due to excellent retention of mechanical properties. The tensile and flexural strength, elongation at break and toughness of the weathered hybrid composites dwarfed that of weathered single-filler composites, even though the mechanical properties of single-filler composites were predominantly more superior to the hybrids before any weathering of the samples took place. It is believed that in hybrid composites, the interparticle cavities, created by low interaction between CaCO_3 fillers and the matrix, would dampen crack propagation from the surface to the interior of the samples.

Inorganic-Organic hybrid aerogels are combined organic molecules with structural elements of inorganic materials. The advantages of these aerogels over inorganic aerogel 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 Figure 4.1 (Hüsing, *et al.*, 1988)

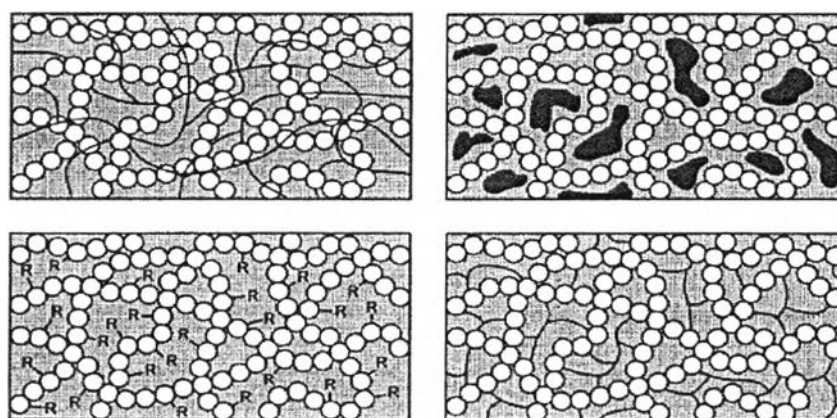


Figure 4.1 Inorganic- organic hybrid networks obtained by sol- gel processing (Hüsing, *et al.*, 1988).

5. Boric acid as a crosslink agent

Polyvinyl alcohol (PVA) polymer has unique chemical and physical properties. These properties come from its hydroxyl groups. The hydrogen bonding between hydroxyl groups was very important in the property of polyvinyl alcohol. For example it has high water solubility, a wide range of crystallinity, and a high crystal modulus. Moreover, the polyvinyl alcohol polymer can react with borate ions to form a polymeric gel. The mechanism of PVA–borate crosslink is believed to be a didiol (two diol) complex, in which two diol units of polyvinyl alcohol chain with one borate ion to form a crosslink.

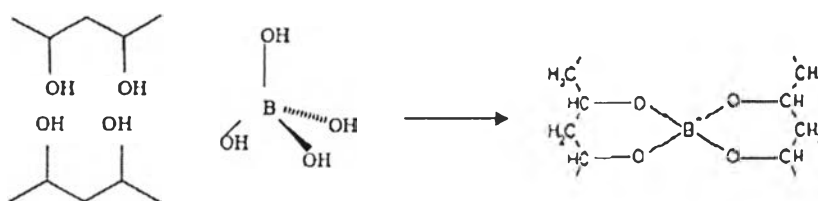


Figure 5.1 The reaction of forming a polymeric gel by boric and PVA

The borax actually dissolves to form boric acid, H_3BO_3 . This boric acid-borate solution is a buffer with a pH of about 9 (basic). Boric acid will accept a hydroxide OH^- from water as indicated

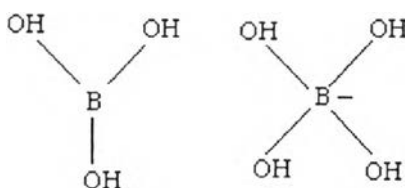


Figure 5.2 shown a chemical equation of boric aqueous and borate ions

Wang *et al* (1999) prepared the elastomeric of polyvinyl alcohol gel from the polyvinyl alcohol polymer, with boric acid as a crosslinking agent, in the mixed solvent of dimethyl sulfoxide and water. From their experimental results show that the viscosity of polyvinyl alcohol solution was increased while a boric acid content increased, in the range of temperature 70°C to 100°C but the viscosity was decreased in the range of 30°C to 70°C. Shibayama *et al* (1988) found that the correlation length remained constant in the gel state and decreased with an increase of temperature in the sol state.

Also, the formation of complexes between polyvinyl alcohol and borate ion has a significant effect on the viscosity behavior of polyvinyl alcohol aqueous. Maerker *et al* (1986) demonstrated that the solution of polyvinyl alcohol with sodium borate exhibited maximum viscosity followed by shear thinning as shear rate was increased also occurring was significant hysteresis phenomenon at higher viscosity. Kurokawa and Ochiai *et al* (1992) studied the viscosity behavior of polyvinyl alcohol aqueous with borate. They found that the viscosity was dependent on the boric acid, PVA. Shibayama *et al* (1988) also found that the relationship of the intrinsic viscosity ratio of polyvinyl alcohol aqueous with borate ion and the equilibrium swelling ratio of gels were in good proportional accordance.

However, most of these studies are concentrated on the behavior of polyvinyl alcohol aqueous gel but not on the polyvinyl alcohol gel from the mixed solvent. Polyvinyl alcohol gel, which is prepared from the mixed solvent of dimethyl sulfoxide (DMSO) and water, has attracted a lot of attention from polymer scientists because of its good transparency, adhesive, and water-holding properties. Some studied have reported that the mechanical properties of polyvinyl alcohol gel from the mixed solvent (dimethyl sulfoxide and water) are the same as those of polyvinyl alcohol gel from a repeated frozen aqueous solution of polyvinyl alcohol. But the time for preparing the polyvinyl alcohol aqueous gel is longer than that of polyvinyl alcohol gel from the mixed solvent. In other words, polyvinyl alcohol gel is much easier to prepare from the mixed solvent.

However, if polyvinyl alcohol gel is used for medical applications, dimethyl sulfoxide is required to be extracted from the gel because of its toxicity. In our previous article, the thermal and rheological properties of polyvinyl alcohol gel in the mixed solvent of dimethyl sulfoxide and water with boric acid as a crosslinking agent were studied.

In 2006, Barros *et al* prepared a preceramic precursor, prepared by condensation reaction from poly(vinyl alcohol) (PVA) and boric acid ($B(OH)_3$) in a B–OH: PVA–OH molar ratio of 1:1, was synthesized, as a potential precursor of lower-temperature route for ceramic material. They found that a boron-containing poly(vinyl alcohol) was easily obtained from the reaction between boric acid. The thermal stability and the activation energy for the degradation process of PVA were determined for the PVAB precursor, and the thermal degradation process was similar to the ones reported for PVA polymers. The activation energy values for the PVAB precursor indicated that the molecular architecture of the precursor was more important in the degradation process than the crosslinking density, but did not show an influence on PVA degradation. However, the crosslinking density showed a strong influence on the ceramic yield.

6. PVA with Freeze/Thaw process

6.1 Introduction of Freeze/Thaw process

To avoid crosslink process which potentially leads to the release of toxic agents, a physical method of gelation and solidification of some polymers, particularly PVA, has been developed. These polymeric materials were first described at the beginning of 1970s but the main mechanisms of PVA cryotropic gel formation were recognized only during the last decade (Watase *et al.*, 1985). The literature data (in general, patents) point to the growing number of areas where cryoPVAGs are proposed for implementation, for example, in medicine as drug delivery carriers or as substitute prosthetists of cartilaginous tissue, ecological engineering for the reinforcement of thawed soils and grounds, microbiology for the creation of solid nutritional media, fishery as artificial baits, the food industry as protective covers for frozen meat or fish, and the development of biomimetic actuators, etc (Peppas *et al.*, 1991).

Hydrogel preparation involves “physical” crosslinking due to crystallite formation. This method address toxicity issues because it does not require the presence of a crosslinking agent. Such physically crosslinked materials also exhibit higher mechanical strength than PVA gels crosslinked by chemical or irradiative techniques because the mechanical load can be distributed along the crystallites of the three-dimensional structure. Aqueous PVA solutions have the unusual characteristic of crystallite formation upon repeated freezing and thawing cycles. The number and stability of these crystallites are increased as the number of freezing/thawing cycles is increased. Some characteristics of these “physically” crosslinked PVA gels include a high degree of swelling in water, a rubbery and elastic nature, and high mechanical strength. In addition, the properties of the gel may depend on the molecular weight of the polymer, the concentration of the aqueous PVA solution, the temperature and time of freezing and thawing, and the number freezing/thawing cycles (Hassan *et al.*, 2000).

6.2 physicochemical bases of cryotropic gelation of PVA solutions

PVA must crosslinked in order to be useful for a variety of applications, specifically in the areas of medicine and pharmaceutical science. A hydrogel can be described as a hydrophilic, crosslink polymer (network). These methods have advantages over the use of chemical crosslinking agent as they do not leave behind toxic.

Overall, solute transport was a function of crystalline fraction of PVA and the mesh size. Figure 6.1 show in more detail the three dimension network structure of swollen, freeze/thawed PVA gels that was proposed in this work. The mesh size is shown between the crystalline regions that serve as the physical crosslinks. A size exclusion phenomenon was demonstrated by this permeation studied which was attributed to the crystallites that create the physical network.

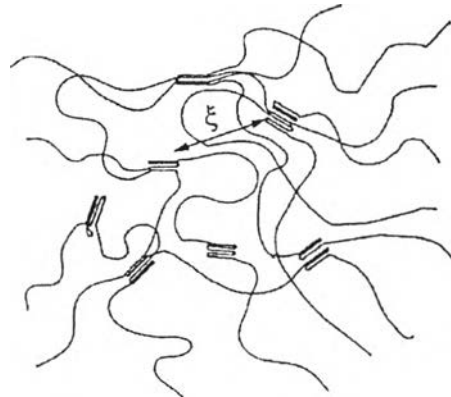


Figure 6.1 Three-dimension network structure of freeze/thawed PVA gels (Peppas *et al.*, 1991).

Poly(vinyl alcohols) are hydrophilic polymers whose concentrated aqueous solutions are capable of gelling *per se* with the formation of a noncovalent spatial network under prolonged storing. The major type of intermolecular links in the junction knots of similar networks in all PVA thermoreversible (physical) gels, including cryoPVAGs, are the hydrogen bonds between OH groups of neighboring polymer chains. The syndiotactic sites in these chains are responsible for the formation of the intermolecular H bonds whereas isotactic sites participate mainly in intramolecular interactions (Fujii *et al.*, 1971).

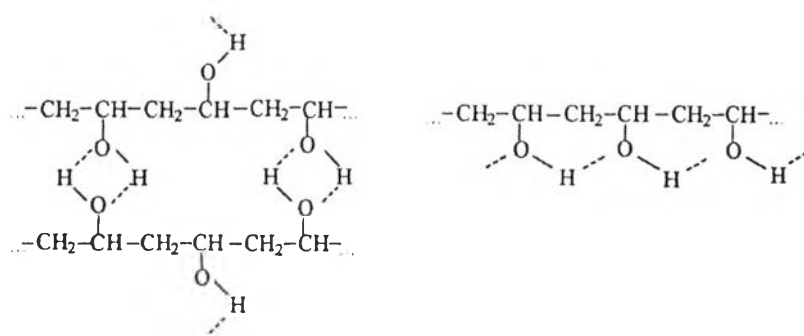


Figure 6.2 Structure of PVA formations (a) syndiotactic sites of hydroxyl group (b) isotactic sites of hydroxyl group (Fujii *et al.*, 1971).

Overall, the crystallinity was found to increase with increasing freezing time and the degree of crystallinity was found to increase with increasing PVA solution concentration (Hassan *et al.*, 2000).

6.3 The using of freeze/thaw process

The majority of publications and patents related to the application of cryoPVAGs mainly deals with cell immobilization thus prepared in a variety of biotechnological processes.

Lozinsky *et al* (1988) prepared Poly vinyl alcohol cryogels by the freeze-thawing of concentrated aqueous solutions of the polymer for the approach of the macroporous mechanically, thermally, chemically, and biologically stable PVA cryogels as carriers of immobilized biomass. Poly vinyl alcohol cryogels employed as matrices for cell immobilization. These carriers possess definite advantages when compared to other hydrogels commonly used for the same purposes. They found the benefits of PVA cryogel that

- (i) It has very high micro- and macroporosities.
- (ii) It is nonbrittle matrix.
- (iii) It has a good thermostability.
- (iv) It highly resistant to biological degradation as well as being of a low sensitivity to culture media compositions.
- (v) PVA itself is a biologically compatible, nontoxic, and readily available low-cost polymer

In 2011, Jiang *et al* ordered to investigate the biopsy precision, PVA materials are adopted in this research to substitute for real tissues *in vitro*. The preparation of transparent PVA hydrogel material and the evaluation of the effect of freeze/thaw cycle number on the hydrogel structure and mechanical property was show in theirs studied. They prepared PVA hydrogel properties for biomedical application which has been proposed as a promising biomaterial suitable for tissue mimicking, vascular cell culturing and vascular implanting.

There are three kinds of samples with the same composition but different freeze/thaw cycles have been prepared. In order to investigate the structure and properties of polyvinyl alcohol hydrogel, micro-structure, mechanical property and deformation measurement have been conducted. As the SEM image comparison results show, with the increase of freeze/thaw cycles, PVA hydrogel revealed the similar micro-structure to porcine liver tissue.

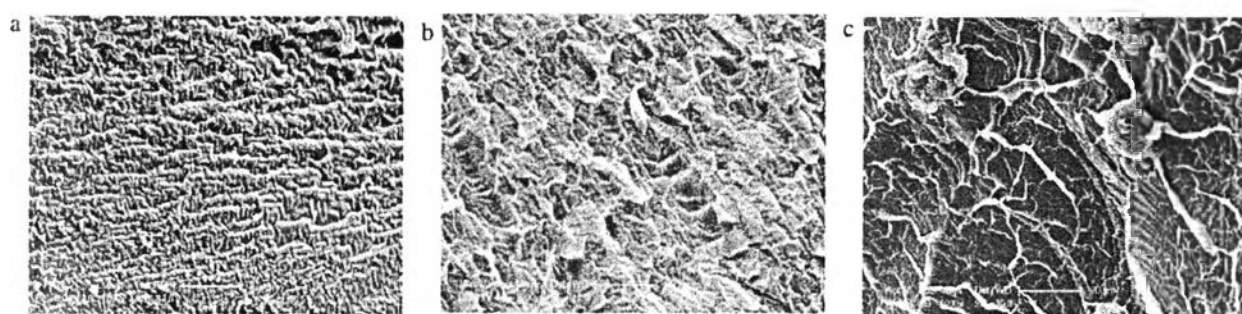


Figure 6.3 SEM images of different freeze–thaw cycles of PVA (a) PVA hydrogel of one freeze/thaw cycle. (b) PVA hydrogel of three freeze–thaw cycles. (c) PVA hydrogel of five freeze–thaw cycles (Jiang *et al.*, 2011).

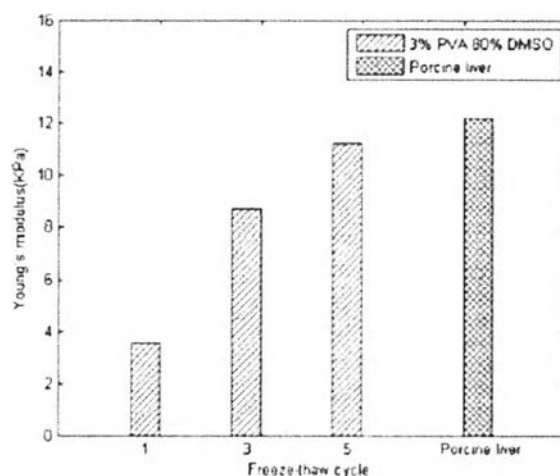


Figure 6.4 The histogram of Young's modulus varied according to different freeze–thaw cycles (Jiang *et al.*, 2011).

With uniaxial tensile strength test, the above composition with a five freeze/thaw cycle sample resulted in Young's modulus similar to that of porcine liver's property. In addition, the number of freeze/thaw cycles of PVA had a marked effect on the stress–strain relationship of PVA hydrogen and its morphological structure.

7. Dimethylglyoxime and Heavy metal

7.1 Dimethylglyoxime and Nickel

The use of Dimethylglyoxime (DMG) as a reagent to detect nickel was discovered by L. A. Chugaev in 1905 for qualitative analysis. DMG is often used as a solution in ethanol. A pair of dmgh⁻ ligands are joined through hydrogen bonds to give a macrocyclic ligand. The most famous complex is the bright red Ni(dmgh)₂, formed by treatment of Ni(II) sources with dmgh₂. This planar complex is very poorly soluble and so precipitates from solution. This method is used for the gravimetric determination of nickel, e.g. in ores

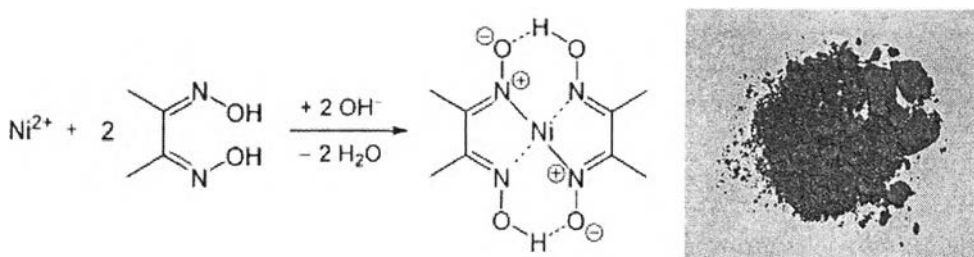


Figure 7.1 shown chemical equation of Dimethylglyoxime and Nickel (Lev Tschugaeff, 1905), Nickel complex (Ni(dmgh)₂).

In 2011, Luxsana Dubas *et al* produced dimethylglyoxime (DMG)/poly(caprolactone) (PCL) blend by using electrospun into fibers. DMG was mixed with PCL in a mixture of N, N-dimethylformamide (DMF) and dichloromethane (DCM) prior electrospinning process. The optical sensor for the nickel detection based on the formation of a red Ni(DMG)₂ complex. The best fibers

were prepared under an electric field of 20 kV and a distance between needle and collector of 20 cm. From scanning electron microscopy (SEM), the average diameter of the fibers remained nearly constant with increasing amount of DMG. The formation of the Ni(DMG)₂ complex was confirmed by Fourier transform infrared spectroscopy (FT-IR). The colorimetric response of the PCL/DMG electrospun fibers were then tested against the nickel ions over a concentration range of 1–10 ppm using reflectance spectroscopy. Good linearity between the reflectance values at 547 nm and the concentrations was obtained ($R^2=0.9925$). These proposed DMG and PCL fibers could be used as the naked-eye sensor for nickel in waste water.

In this work, we demonstrated that the PCL electrospun fibers containing dimethylglyoxime (DMG) could be used as a novel optical sensor for the analysis of nickel (II) ion concentration by dipping into the solution. The optical response of the sensor is based on the well known reaction between nickel and DMG leading to the formation of a red complex of Ni(DMG)₂ with an absorbance peak at 547 nm. Here, DMG was directly blended with PCL in a solvent and then electrospun into fibers.

The morphology and composition of the blended fibers were color change when exposed to various concentrations of nickel solutions as low as 1–10 ppm of nickel in water. This sensor can be used in the determination of nickel ions concentration in waste water from batteries or nickel alloy manufacturers. The simple dipping method detection makes it easy to be used in the field for example to monitor river contaminations. This developed sensor has shown a good advantage when compared to other analytical techniques in this aspect.

7.2 Dimethylglyoxime and Cobalt

The nitrogen atoms in dmgH₂ and its complexes are sp² hybridized (Girolami G *et al.*, 1999). Because of the planarity of the resulting ligand, the macrocycle [dmgH]₂²⁻ resembles some biologically important macrocyclic ligands, as found for example in vitamin B12 and myoglobin. A well known family of model complexes, the cobaloximes, have the formula CoR(dmgh)₂L, where R is an alkyl group and L is typically pyridine. In such complexes, L and R occupy “axial” positions on the

cobalt, perpendicular to the plane of the dmgH_2 . One of the examples of cobaloxime is chloro(pyridine)cobaloxime.

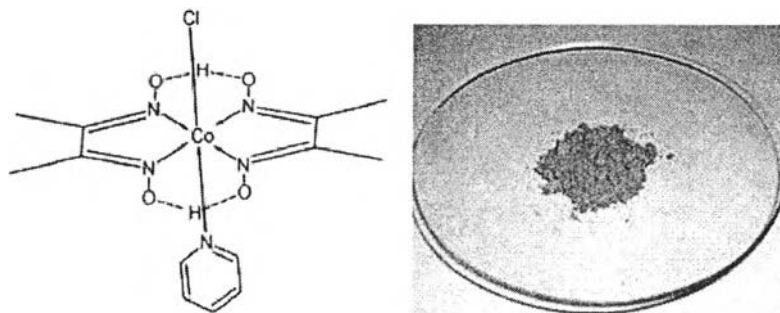


Figure 7.2 shown structure of chloro(pyridine)cobaloxime and sample of chloro(pyridine)cobaloxime.

8. Aerogels

8.1 Introduction of Aerogels

Aerogels are a special class of nanoporous materials with growing interest in biomedical and pharmaceutical applications due to their open pore structure and high surface area. Aerogel technology provides high added-value lightweight materials with outstanding surface area and open porosity, suitable for loading with active compounds (Rolison, 2003, Smirnova *et al.*, 2003 and Smirnova *et al.*, 2004). Aerogels are obtained from wet gels by using a suitable drying technology, usually a supercritical drying process, able to avoid the pore collapse phenomenon and keep intact the porous texture of the wet material.

The physical properties and structures of the aerogels depend on precursors and the sol-gel process parameters such as type and concentration of precursor, type of solvent, type of catalyst, temperature, pH, time, type of drying etc (Aegerter *et al.*, 2011).

Polysaccharide-based aerogels result in highly porous and lightweight with high surface area, able to provide enhanced drug bioavailability and drug loading capacity. There are three type of drying method for aerogels (Hüsing *et al.*, 1998).

a) 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 which without collapsing of the pore structure. Supercritical drying can be performed along pathway A or B as shown in Figure 8.1 (Hüsing *et al.*, 1998).

b) Ambient-Pressure Drying

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

c) Freeze-Drying

Freeze drying is one of drying method for aerogel which this method is eliminate liquid/gas interfaces problem causing collapsing of network. Freeze drying process is to freeze the liquid pore then sublimed under vacuum. The temperature is raised to allow the ice sublimed as shown in Figure 8.1. The main problem with this technique is nucleation and growth of 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 (Hüsing *et al.*, 1998 and Aegerter *et al.*, 2011).

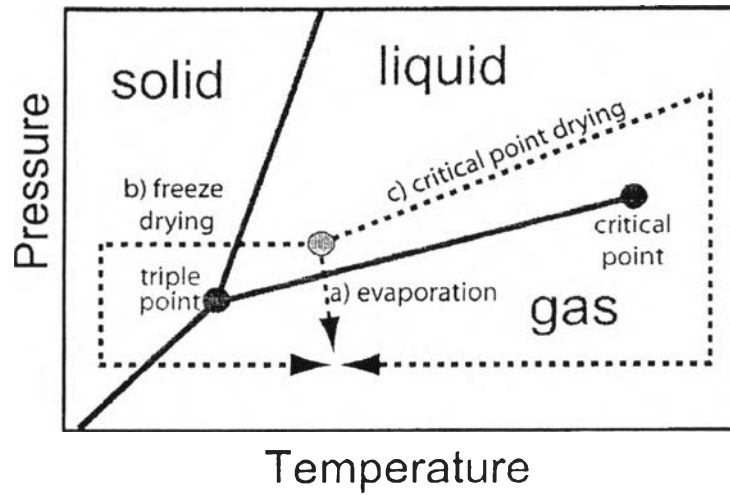


Figure 8.1 Principal of (a) supercritical drying and (b) freeze-drying (Bryning, 2007).

8.2 Application of Aerogels

Nowadays, Aerogel technology plays the important role in the industry. Many researchers have been studied on aerogel technology and there are continuously increasing publications about aerogel as shown in Figure 8.2.

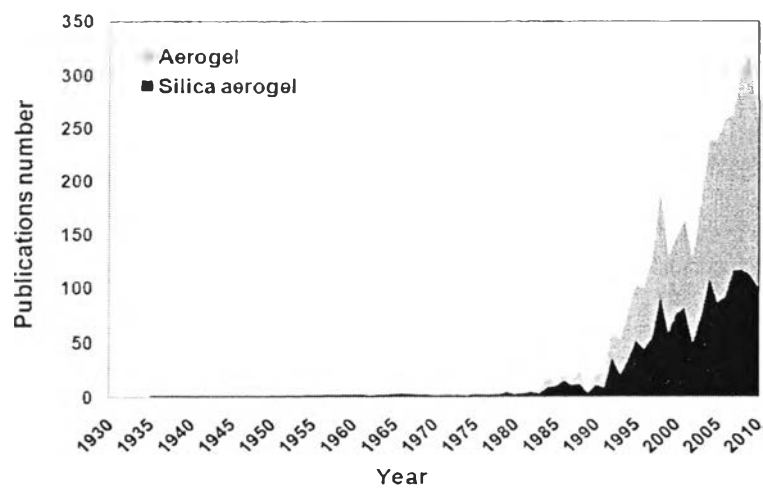


Figure 8.2 Publications number of aerogel (Alnaief, 2011).

Aerogels are used for many applications which based on specific properties and potential applications for aerogels are wide ranging and unlimited as shown in Table 8.3. (Hrubesh, 1998)

Table 8.3 Identifications of aerogel properties, features and applications (Hrubesh, 1998)

Property	Features	Applications
Thermal conductivity	<ul style="list-style-type: none"> -best insulating solid -transparent -high temperature -light weight 	<ul style="list-style-type: none"> -architectural and appliance insulation, portable cooler, transport vehicles, pipe, cryogenic, skylight -Space vehicles and probes, casting molds
Density and Porosity	<ul style="list-style-type: none"> -lightest synthetic solid -homogeneous -high specific surf. area -multiple compositions 	<ul style="list-style-type: none"> -catalysts, sorbers, sensors, fuel storage, ion exchange -targets for ICF, X-ray lasers
Optical	<ul style="list-style-type: none"> -low refractive index solid -transparent - multiple compositions 	<ul style="list-style-type: none"> -lightweight optics, light guides, special effect optics
Acoustic	<ul style="list-style-type: none"> -lowest sound speed 	<ul style="list-style-type: none"> -impedance matchers for transducers, range finders, speakers
Mechanical	<ul style="list-style-type: none"> -elastic -lightweight 	<ul style="list-style-type: none"> -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
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