

CHAPTER II

LITERATURE REVIEW

2.1 Climate Change

Climate change is caused by the drastic increase in greenhouse gases in the atmosphere. Thailand is not spared from this change, which results in long and hotter summers, and shorter rainy seasons. This recent development has made water storage and management even more important, especially in semi-arid countries. Since most of these countries rely heavily on agriculture. Potential water shortage threatens the daily life of people living in these countries, as without sufficient supply of clean fresh water, they are not able to produce crops.

Most semi-arid countries have sandy soils or other infertile soils with low water holding capacity. A good soil is important for plant growth. The main function of soil is to store moisture and nutrients, and supply them to the growing plants. Within the soil, water is held in the soil pores (the space between the soil particles) as shown in the Figure 1. Evaporation from the soil surface, transpiration by plants and deep percolation effect, reduce the soil moisture. If the water content becomes too low, plants become stressed and eventually die.

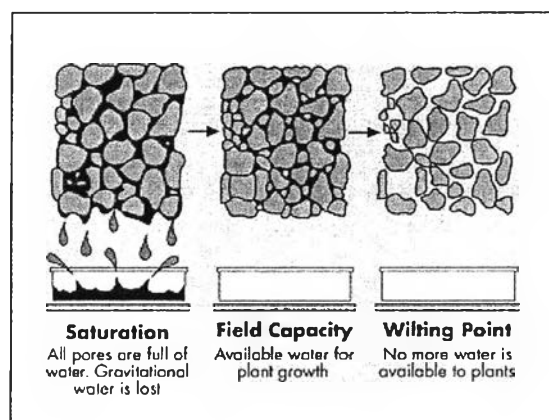


Figure 2.1 Stages of water holding.

2.2 Porous Materials

In 1997, D. Jhurry reviewed the need of improving the physical properties of agriculturally managed soils. Polymers were developed to improve the physical properties of soils, such as an increased water-holding capacity, more efficient use of irrigation water, enhanced soil permeability, better infiltration rates, reduced irrigation frequency, reduced compaction tendency, and increased performance of the crops. But the initial products were costly, the application methods were complex, and the distribution within the soil was poor. This led to the development of water-soluble polymeric soil conditioners. Polyacrylamide (PAM) is one of most widely employed soil conditioners. In 1986, Wallace *et al.* showed that a mixture of galactomannan, extracted from guar bean, and polyacrylamide resulted in an additive response when applied to certain soils.

Jhurry *et al.* (1992) developed linear vinyl polymers containing sucrose in the side chains. The synthesis of high molar mass hydrosoluble poly(O-methacryloysucrose) has thus been achieved, and has been used as soil conditioner.

Super-absorbent polymers have shown encouraging results by reducing irrigation water consumption, the death rate of plants, improve fertilizer retention in the soil and increase plant growth (Puoci, 2008). Moreover, the use of hydrogels leads to an increased efficiency in terms of water usage, where it would otherwise leach beyond the root zone. During hot days, the roots of plants pull out and deplete water from their surroundings, thus causing further stress on the plants. While increasing the amount of available moisture, hydrogels help reduce water stress of plants resulting in increased growth and plant performance (El-Hady *et al.* 1981; Pill and Jacono 1984; Baker 1991). In 2004, El-Rehim described that superabsorbent hydrogels can improve the properties of sandy soils, because they can absorb and retain water in the magnitude of one thousand times to their own weight. This lead to a reduced watering frequency, and enhanced the water retention of the soil matrix, which resulted in an increase in plant growth and performance. However, due to the poor degree of cross-linking in hydrogels, which on the other hand allows high water retention and swelling; hydrogels readily degrade and wash away.

2.3 Poly(High Internal Phase Emulsion)

Recently, a novel highly porous polymer was introduced. It is synthesized via high internal phase emulsions (HIPEs) polymerization, giving the material an open, porous structure. Emulsions are composed of a droplet phase (also called: disperse, or aqueous phase) and a continuous phase (organic phase). The droplet phase occupies more than 70% of the total volume. Polymerization occurs around emulsion droplets, which create voids in the final material, and the continuous phase solidifies around the droplet phase. Furthermore, there are small windows between voids, these are interconnecting pores (Neil, 2004), Figure 2 shows the characteristic structure of a polyHIPE porous foam. PolyHIPEs have found application in areas, such as ion exchange, filter, sensors, cell culturing, tissue engineering and agriculture.

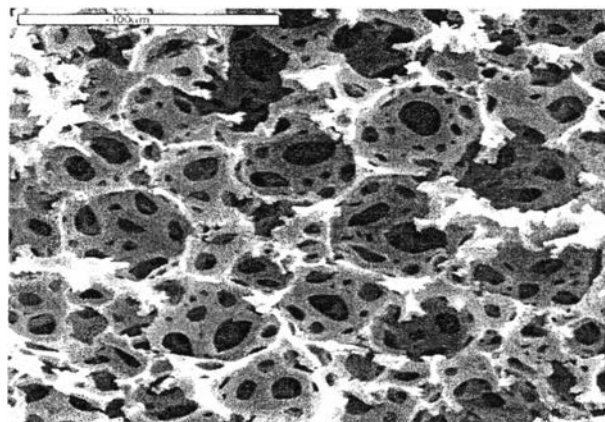


Figure 2.2 Characteristic structure of a polyHIPE.

In order to achieve a stable emulsion, a surfactant must lower the interfacial tension between the two phases, by forming a rigid interfacial film which must be rapidly adsorb at the interface (Ford *et al.*, 1966). Ionic surfactants stabilize HIPEs through electrostatic repulsion and nonionic surfactants stabilize HIPEs through steric hinderance. The strength of the interfacial film is enhanced by the ability of the surfactant to pack closely. A surfactant blend is often able to pack more effectively.

Salts can enhance the ability of surfactants to pack into a more stable structure. Pons *et al.* (1992) found that the addition of NaCl can enhance the rigidity of the interfacial film in water in oil (W/O) HIPEs. It can also enhance the emulsion stability by inhibiting Ostwald ripening, a process by which large droplets grow at the expense of smaller ones. The addition of salts, reduces the solubility of the aqueous phase in the oil phase, thus reducing the attractive forces between the droplets (Kizling *et al.*, 1990)

Considering the interfacial free energy for both W/O and O/W systems is important for the stability of HIPEs. Chen *et al.* (1990) have shown that in W/O HIPEs, the hydrophobicity of the oil phase and the hydrophilicity of the aqueous phase are high the interfacial tension and effect the stability of HIPE formation. They further found that the viscosity of the continuous phase also affected the stability of HIPEs. With increasing viscosity, the amount of disperse phase decreases (Chen *et al.*, 1991). For agricultural applications, Akay *et.al.* (2012) showed a regulated water and fertilizer delivery and enhance root-bacterium-nature-nutrient interaction, by synthesizing sulfonated polyHIPEs as potential soil additive and Synthetic Rhizosphere (SRS)-media

2.4 Polystyrene (PS)

Polystyrene is a vinyl polymer, produced from free radical vinyl polymerization of petroleum based styrene monomers, a hydrocarbon material. Its structure consists of a long hydrocarbon chain with phenyl groups (aromatic rings) besides, along the chain.

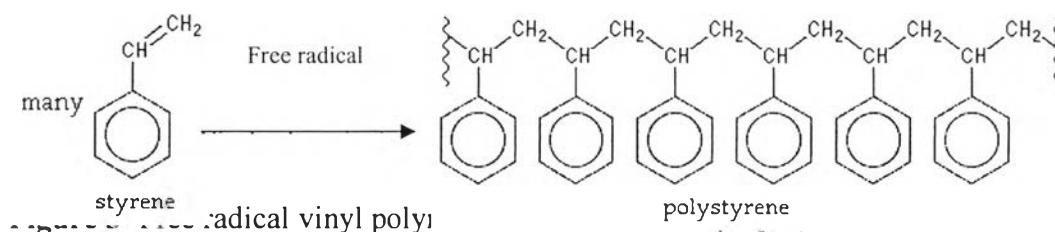


Figure 2.3 Free radical vinyl polymerization reaction of polystyrene.

Polystyrene is classified as a thermoplastic material, since it turns into liquid when heated above 185°F (85°C) and freezes to a rigid state when cooled sufficiently, which means that at room temperature it is solid. Due to the many aromatic rings in its structure, polystyrene is a material that possesses high fire resistance, good resistance to acids and bases, good electric insulating properties, high shock-resistance, and excellent surface characteristics. Due to these outstanding properties, polystyrene can be considered as a unique and potentially useful material. Moreover, polystyrene is transparent, and can be easily colored and fabricated. A further advantage of polystyrene is that it is an inexpensive raw material. Hence, it is an excellent material for producing consumer products.

2.5 Ethylene Glycol Dimethacrylate (EGDMA)

Ethylene Glycol Dimethacrylate or 2-(2-Methyl-acryloyloxy)ethyl 2-methyl-acrylate (IUPAC name) is a diester produced from two equivalents of methacrylic acid and one equivalent of ethylene glycol. It is a clear liquid and typically used as a functional monomer for polymers as well as a free radical copolymer crosslinking agent (high purity crosslinker with bridging/specialty capability) between the molecular chains of polymers and elastomers.

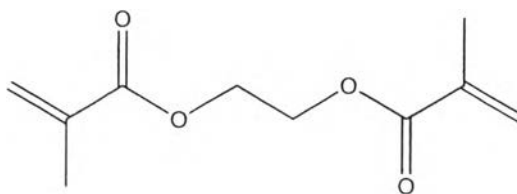


Figure 2.4 Structure of Ethylene Glycol Dimethacrylate.

2.6 Divinylbenzene (DVB)

Divinylbenzene or DVB composes of a benzene ring interact with two vinyl groups, is a crosslink agent. DVB can be used as a reactive monomer in polyester

resins and can be polymerized with styrene to form copolymer S-DVB, used for the ion exchange application.

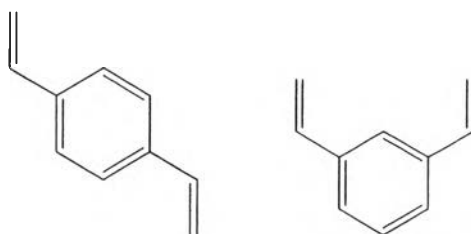


Figure 2.5 Structure of Divinylbenzene.

2.7 Polystyrenesulfonate (PSS)

Polystyrenesulfonate or PSS are polystyrene sulfonic acid polysalts, usually in form of sodium and calcium. PSS is polyanion, white powder and soluble in water. They have widely used as ion-exchange resins.

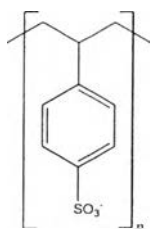


Figure 2.6 Structure of Polystyrenesulfonate.

2.8 Poly(diallyldimethylammonium chloride) (PDADMAC)

Polydiallyldimethylammonium chloride (shortened polyDADMAC or polyDDA) is a homopolymer of diallyldimethylammonium chloride (DADMAC). The molecular weight of polyDADMAC is typically in the range of hundreds of thousands of grams per mole, and even up to a million for some products. PolyDADMAC is usually delivered as a liquid concentrate having a solids level in the range of 10 to 50%. It is a high charge density cationic polymer. The charge density makes it well suited for flocculation.

PolyDADMAC is used as a coagulant in water purification. It is effective in coagulating and flocculating inorganic and organic particles such as silt, clay, algae, bacteria and viruses. At high concentrations the organic polymer can remove natural organic matter such as humic and fulvic acids resulting in fewer disinfection byproduct precursors and less color.

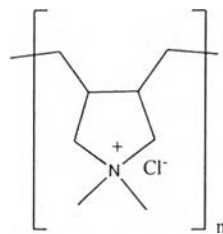


Figure 2.7 Structure of Poly(diallyldimethylammonium chloride).

2.9 Poly(acrylic acid) (PAA)

Poly(acrylic acid) or PAA or Cabomer is synthetic high molecular weight of acrylic acid. PAA is a polyanion in water solution at pH7, side chains will lose protons and receive negative charges. This makes PAA polyelectrolytes. PAA can absorb and retain water and swell many times.

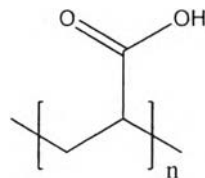


Figure 2.8 Structure of Poly(acrylic acid).

3.0 Alginic acid (ALG)

Alginic acid (ALG) or align or alginate is an anionic polysaccharide. It can rapidly absorb water when it was extracted form. ALG has a range of color from

white to yellowish-brown. It absorbs water quickly. The chemical compound of sodium alginate is the sodium salt of alginic acid. Its formula is $\text{NaC}_6\text{H}_7\text{O}_6$.

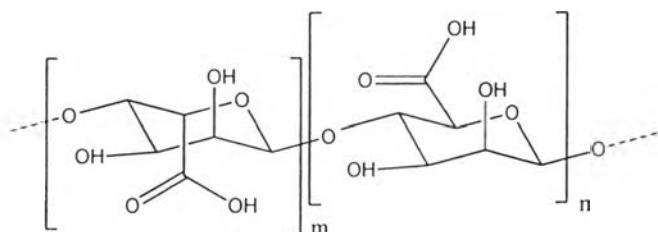


Figure 2.9 Structure of Alginic acid.

3.1 Chitosan (CTS)

Chitosan (CTS) is a linear polysaccharide composed of distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating shrimp and other crustacean shells with the alkali sodium hydroxide.

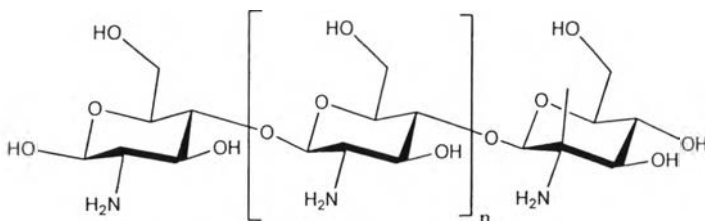


Figure 2.10 Structure of Chitosan.

3.2 Surface Modification

3.2.1 Functionalization

PolyHIPE can be modified to a variety of applications such as column filtration/separation, catalyst support, media for tissue engineering and soil addition (Fabrice *et al.*, 2012; Burke *et al.*, 2010; Haifei and Andrew, 2005). Most polyHIPEs are hydrophobic; produced by water-in-oil (W/O) system. However, there are two

methods to synthesis of hydrophilic polyHIPE, the first method is direct synthesis hydrophilic polyHIPE in an oil-in-water (O/W) system such acrylamide (Haifei and Andrew, 2002) or acrylic acid (Krajnc *et al.*, 2005). Another method is modified surface of polyHIPE by the addition of a functionalizable comonomer, such as vinylbenzyl chloride, on a HIPE base on a non-functionalizable monomer, such as styrene or divinylbenzene (Shulamit *et al.*, 2009; Cameron and Sherrington, 1996).

In 2009, Shulamit and coworker have to functionalised on polyHIPE but different to previous work. They synthesized polyHIPE with tBA which is hydrophobic then hydrolyzed it to achieve hydrophilicity, their ability on absorb water. Fabric *et al.* (2012), Functional polyHIPE by surface-initiated atom transfer radical polymerization (ATRP), Functionalized surface of polyHIPE with amino group (-NH₂). They found a dense and homogeneous coating on surface. This result show a high versatile that good for bioseparation application.

3.2.2 Layer-by-Layer Technique

Electrostatic self-assembly is a simple, yet versatile and environmentally friendly technique. This technique has been widely used in different areas and recently it has also been used to make nano-structured separating layers for composite polyelectrolyte pervaporation membranes. Non-porous substrates are usually employed for electrostatic self-assembly depositions, but porous substrates have to be used for membrane applications because the composite membranes fabricated with non-porous substrates will have low permeation fluxes. When porous substrates were used to make composite membranes for pervaporation, it was reported that 60 double-layers were needed to get a membrane with suitable separation performance (Zhaoqi, 2006).

The LBL method has received much attention in the field of electrochemistry as a very promising tool for the fabrication of nanostructured films with high organisation at the nanoscale level fabricated films through specific interactions of organic functional groups for multilayer growth, and the films deposited onto a solid substrate were obtained with high stability. For the growth of multilayer films, the adsorption occurred as a result of alternating the immersion process of a solid substrate (for example, quartz and hydrophilic or hydrophobic

glasses) in a cationic and anionic polyelectrolyte solution and the excess of weakly adsorbed polyelectrolyte is washed in a solvent solution and dried with nitrogen gas/air flow (Fig. 11) (Rodrigo *et al.*, 2012)

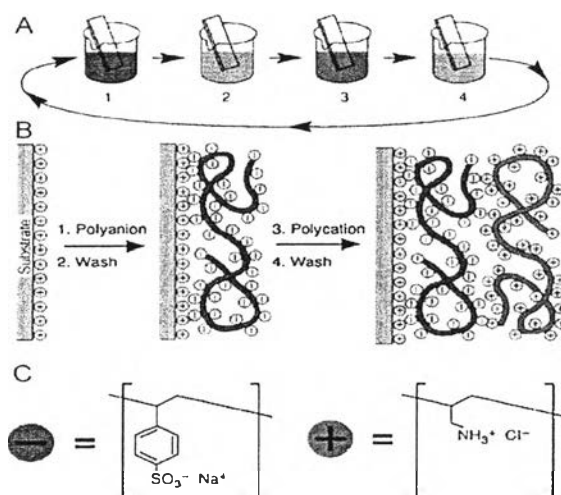


Figure 2.11 Schematic of the film deposition process using slides and beakers.

(A) Steps 1 and 3 represent the adsorption of a polyanion and polycation, respectively, and steps 2 and 4 are washing steps. The four steps are the basic buildup sequence for the simplest film architecture, (A/B) $_n$. The construction of more complex film architectures requires only additional beakers and a different deposition sequence. (B) Simplified molecular picture of the first two adsorption steps, depicting film deposition starting with a positively charged substrate. Counterions are omitted for clarity. The polyion conformation and layer interpenetration are an idealisation of the surface charge reversal with each adsorption step. (C) Chemical structures of two typical polyions, the sodium salt of poly(styrene sulfonate) and poly(allylamine hydrochloride) (Rodrigo *et al.*, 2012).

The LBL method becomes very advantageous because numerous different materials can be employed in the fabrication of films. Also, LBL is more versatile than other fabrication techniques and provides the possibility of using a large range of different materials in films construction, including polyelectrolytes, dendrimers (DENS), carbon materials, and many others. Moreover, parameters such as roughness, thickness, and porosity of films can be controlled by changing

experimental conditions such as pH, temperature, polyelectrolyte concentration, and ionic strength of the media (Rodrigo *et al.*, 2012).

Polymer materials have been coated with PEM as a top coating covering the porosity. In this work we use a syringe to flow the PEM through the polyHIPE materials, especially coating on the cell wall.

2.5 Water Absorption

PolyHIPEs are able to absorb large quantities of liquid through capillary action. Absorption begins when the polyHIPE is immersed into a liquid and the process can continue until all the air, within the voids, has been displaced by the liquid. The tendency of a particular type of polyHIPE to absorb a particular liquid depends on the interfacial tension between the two of them, especially on the contact angle. When polystyrene-based polyHIPEs absorb toluene, they swell. They will also absorb a bit of methanol and not absorbed water at all (Neil, 2011).

The study of water absorption of poly(methyl methacrylate)PMMA with varied monomers and temperatures, showed that the maximum water uptake was increased as the increase of monomers concentration and not influenced by the temperature. The rates of water absorption were obtained using Fick's law of diffusion. At the early stage of the diffusion process is presented as follows.

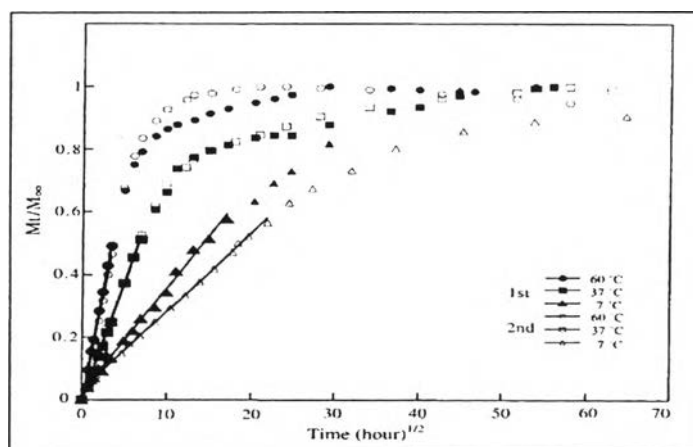


Figure 2.12 Plots of the water uptake ratio.

The results show, that there was no relationship between the maximum water uptake and the diffusion coefficient. To analyze the temperature dependency of the diffusion coefficient, D , the values were plotted according to Arrhenius equation.

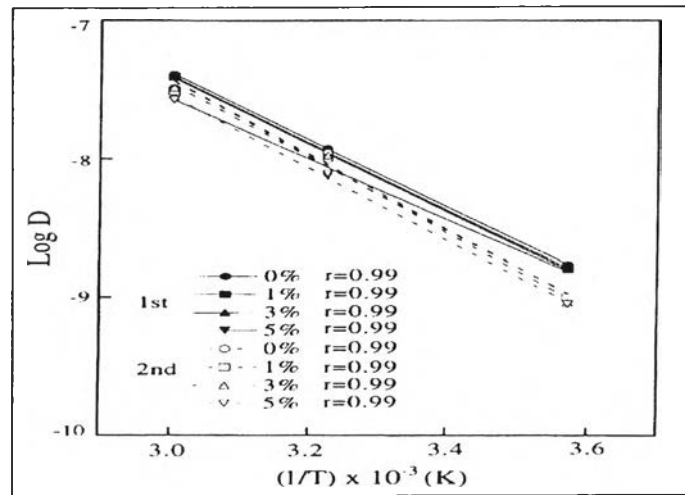


Figure 2.13 Plots of the diffusion coefficient (D) versus the absolute temperature (T).

The study show, that the maximum water uptake was not influenced by the temperature, however, the diffusion coefficient increased with rising temperatures, as well as the necessary activation energy. The first absorption was slower than the second, due to the existence of residual monomers (Masako, 2003).

Burke *et al.*, (2010) studied the water adsorption within the structure of polyHIPEs by using sample disks 24 mm in diameter and 4 mm thickness. These will be fully dried and weighted before being immersed into water, at room temperature for 30 s. They were then removed from the water, dabbed dry with tissue paper to remove water from the surface, and reweighed to determine the water adsorption by using the following equation:

$$\text{Water adsorption capacity} = (W_s - W_d) / W_d \quad (1)$$

Where W_s and W_d are the weights of the soaked and dry polyHIPEs, respectively.

Anatoly *et al.* (2001), study the influence of compositions and surface treatment to interact with water, they found polyHIPE wash in water at 70°C increased water absorption capacity due to reduce residual salt and addition of fluorinated comonomer enhanced hydrophilicity, thus water absorb.

In 2012, Akey *et al.* studied the water adsorption capacity of synthetic rhizosphere media polymers (SRS-media polymer), functionalization by sulphonation and neutralization which resulted in a nanostructure of cross linked, hydrophilic elastic ionic micro-porous material, generally known as PolyHIPE Polymers (PHPs). They illustrated that, if PHP had pores of small size, it would restrain them from swelling upon contact with water. Both, the rate of adsorption and total absorption capacity are low. In the case of large pores (diameter $> 50 \mu\text{m}$), the water uptake and capacity were much greater due to swelling upon absorption. However, it was found that these SRS-media-PHPs did not allow root penetration.