CHAPTER II
LITERATURE REVIEW

Nowadays, more than a half area of Thailand is threatened by drought. To re-solve it, improving the quality of soils is the way of choice. For several years, pol-yHIPEs have been an interesting material as soil additive, which have the ability ad-sorb water several times their own weight and slowly release to the roots under the stress condition without any further irrigation.

2.1 PolyHIPEs

PolyHIPEs (high internal phase emulsion) polymers are highly porous mate-rials that have been known for several years. The internal or dispersed phase occu-pies more than 74% of the total volume and commonly contains water, an initiator and stabilizers. The external or continuous phase generally constitutes for less than 26% of the total volume. It usually consists of the monomer, a crosslinking comon-omer and emulsifier (surfactant). By polymerizing the continuous phase, the emul-sion droplets are embedded in the resulting material (Cameron et al., 1996).

The unique feature of polyHIPEs is its highly porous structure, which can be synthesized via emulsion templating. This provides a flexible and simple method for the fabrication of macroporous materials.

Under suitable conditions, interconnected pores are created between adjacent emulsion droplets, which then allow the dispersed phase to be entirely removed by drying in a convection oven.
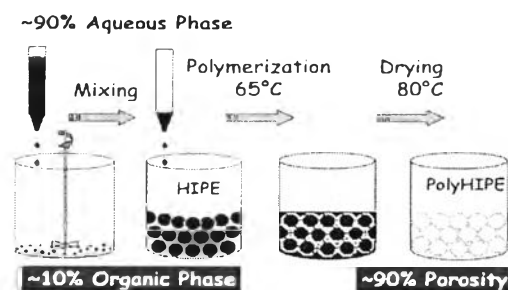

Figure 2.1: Schematic illustration of typical polyHIPE synthesis. *(Michael S., 2008)*

For better understanding, some important wordings that will be used are defined here. Firstly, 'Pores' corresponds to the big spherical cavities within the material. Secondly, the small holes between adjacent pores and referred to as 'interconnected pores'.
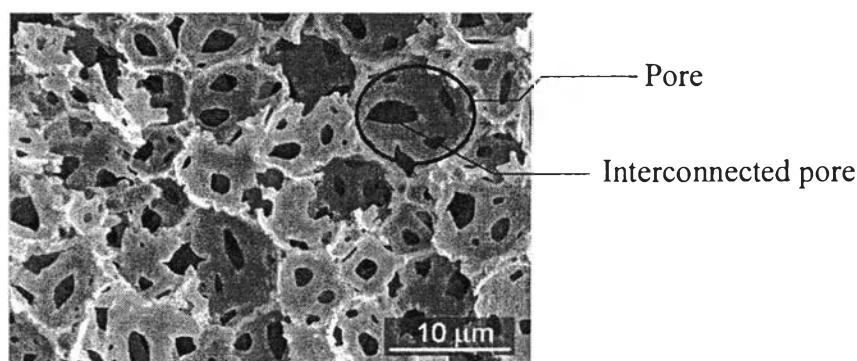

Figure 2.2: SEM picture showing typical structure of polyHIPE monolith. Pores and interconnected pores are marked. *(Michael S., 2008)*

PolyHIPEs have many great properties, such as high porosity, high permeability, surface area up to 700 m^2/g, low density (down to 0.03 g/cm^3) and the ability to adsorb large amounts of liquid, resulting from their highly interconnected, open-cell structure. Due to these characteristics, highly interconnected macroporous materials are popular in applications such as cell culture applications (Lee *et al.*, 1992), gene therapy (Cavanagh *et al.*, 2001), enzyme immobilization (Hsuanyu, 2002), separation medium (Bhumgara *et al.*, 1995), ion exchange (Wakeman *et al.*, 1998), electrode (Brown *et al.*, 1999), drug delivery (Landgraf *et al.*, 2003), and catalysis support (*Sunstorm research corporation*). A major advantage of introducing large macropores into such materials is that it enhances the mass transport of large molecules, especially in viscous systems (Sergienko *et al.*, 2002).

2.2 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.
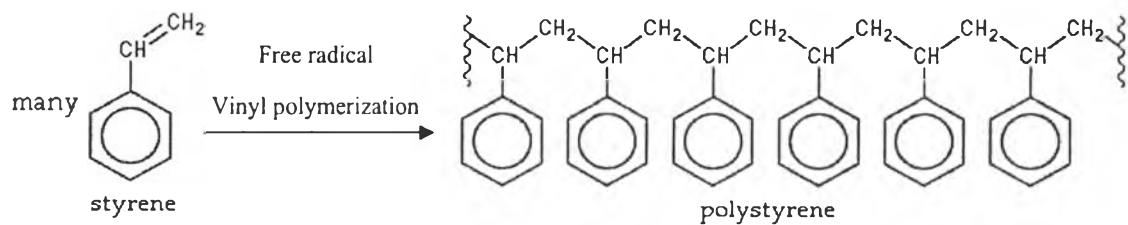

Figure 2.3: Free radical vinyl polymerization reaction of polystyrene.

(en.wikipedia.org/wiki/Polystyrene: polymerization)

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.

2.3 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.
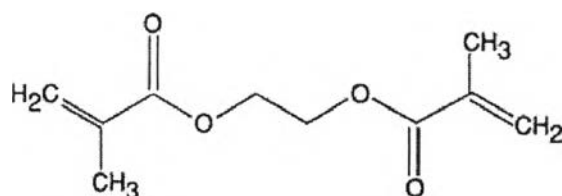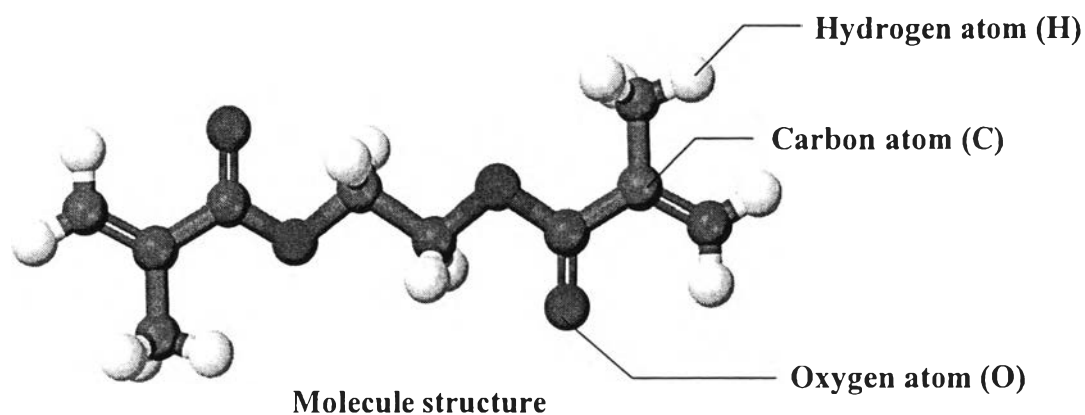

Linear molecule of EGDMA

Molecule structure

Figure 2.4: Structure of Ethylene Glycol Dimethacrylate.

(en.wikipedia.org/wiki/Ethylene_glycol_dimethacrylate)

2.4 Water Adsorption Capacity of PolyHIPEs

Water adsorption is an interesting ability of polyHIPEs, which allows them to be used efficiently in agriculture. In order to indicate the performance of a material, water adsorption capacity is used to determine the amount of water adsorbed under specified conditions. Factors affecting water adsorption include: type of raw material, additives, temperature and length of exposure.

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:

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

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

2.5 Literature review

In order to combat agricultural water shortages, several approaches have been adopted, e.g. soil additives with high water absorption capacity. Crosslinked polymers that absorb and retain fluids hundreds of times their own weight which are called superabsorbents, (Bakass *et al.*, 2002) were interested in studying the absorption and desorption of liquid water by a these polymers. The focus of this work was the effect of the polymeric material on the quality of the crops, as soil dries due to stopped irrigation, by studying the drying kinetics of the gel and soil, under controlled pressures and temperatures. The result showed that these polymers have certain possible applications in agricultural production systems and soil additives, since they are able to preserve water in the soil for a longer period of time, by reducing water losses due to infiltration and evaporation.

However, due to poor cross-linking, which on the other hand allows high water retention and swelling, superabsorbents readily degraded and wash away, and requiring replenishment (Akay *et al.*, 2012). Barby *et al.*, (1982), researchers at Unile-

ver, have patented a process for the preparation of highly porous, cross-linked polymeric materials by polymerizing the external phase of a HIPE (high internal phase emulsion). These materials were branded polyHIPE polymers (PHPs) and thus, presented plentiful advantages over superabsorbents.

As soil additives, PHPs enhance plant growth and crop yield (Akay *et al.*, 2009). Further advantages are: reduced costs, controlled size of the material, pore microstructure (i.e., pore and interconnected size, pore volume, and pore wall chemistry), ability to include biologically or chemically active components (e.g., bacteria or fertilizer), control of rigidity, and high water adsorption capacity.

Commonly, HIPE stability is affected by various factors, including the molecular structures of the components comprising the phases and of the surfactant, the surfactant content, the dispersed phase content (Williams *et al.*, 1990), the temperature (Pons *et al.*, 1993), and the presence of stabilizing salts (Pons *et al.*, 1992). The nature of the surfactant is critical to the stability of a major phase dispersed within a minor phase. The surfactant used to stabilize a HIPE should, therefore, be completely insoluble in the dispersed phase to prevent phase separation and/or phase inversion. A nonionic surfactant with a low hydrophilic lipophilic balance (HLB), such as sorbitan monooleate (Span 80) with its HLB of 4.3, is needed to form a stable W/O HIPE.

The potential applications of PHPs in agriculture were studied by Burke *et al.*, (2010). They investigated the transformation of hydrophobic styrene/DVB PHP to a hydrophilic form, by using microwave sulfonation. The rigid form (pore size = 20 μm) of sulfonated PHP had a lower water-uptake capacity (ca. 10-fold of its own weight) compared to the large-pore-size spongy form (pore size = 150 μm, water-uptake capacity = 18 fold). The results showed that the rigid sulfonated PHPs produced no significant increase in the yield compared to the control but, the spongy sulfonated PHPs greatly enhanced the yield. Especially, under semiarid and arid conditions, the yields in biomass could be enhanced by about 140% and 300%, respectively compared to the control. Moreover, They also studied the effect of DVB content on the water adsorption capacity. This was found that at increasing in DVB content from 2%-10%, the water adsorption capacity increased.

There are several researches about increasing the average pore and interconnected pore size in the resulting porous material. Carnachan *et al.*, (2006) did research in on tailoring the morphology of polystyrene-based emulsion-templated (PolyHIPE) materials. In this work, the oil phase consisted of styrene, 2-ethylhexyl acrylate, divinylbenzene and the surfactant sorbitan monooleate (span 80). The effect of the temperature of the aqueous phase, the presence of organic additives: tetrahydrofuran(THF), methanol and poly(ethylene glycol) (PEG), and surfactant concentration were studied, with the focus on the effects on the morphology of polyHIPEs. The results showed that an increase in the temperature of the aqueous phase prior to emulsification, can lead to a material with a larger average pores and interconnected pore size. It is suggested, that this increasing in size is due to coalescence, caused either by increased droplet collision or increased surfactant solubility in the organic phase. They further showed that the presence of additives or co-solvents in the aqueous phase can lead to a material with a higher average pore and interconnected pore size, this effect was greatest when THF was used as an additive and is most likely due to Ostwald ripening. On the other hand, increasing the surfactant concentration from 20 to 30% (w/w) in emulsions prepared with additives caused only small changes in the size of the pores. This suggests that depletion of surfactant from the interface in the presence of an organic additive only plays a minor role in the morphology of polyHIPEs.

These results were also confirmed by the previous work of Hayman *et al.*, (2005) who added small quantities of water miscible organic solvents in the emulsion aqueous phase of S/DVB HIPEs focusing on the mean pore diameters. They found that the addition of around 1% (v/v) of tetrahydrofuran (THF) to the aqueous phase resulted in foams with pore diameters in the range 50–100 μm (5-20 μm without additive), as determined by scanning electron microscopy. The increase in pore size is due to the fact, that the water miscible organic solvent, THF, is capable of partitioning between the two phases. Thus, helping to promote the transport of water throughout the organic phase, this enhances emulsion destabilization due to Ostwald ripening.

The effect of operating conditions on the pore and interconnected size were investigated by Akay *et al.*, (2002). The oil phase contained styrene, DVB and span

80, while the aqueous phase contained water and potassium persulphate. The temperature of the aqueous phase, and the dosing time were ranged from -1.0 to 80 °C and from 25 to 40 seconds respectively. This work indicated that both, an increase in the temperature of the aqueous phase, and a longer dosing time can expand the pore size of polyHIPEs. Furthermore, it was suggested that water soluble polymers could have an effect on pore and interconnected size, this might be due to controlled pore coalescence. The results showed that, the higher the relative molecular mass of the water-soluble polymers, the larger the pore size of the resulting material. Likewise, increasing the wt-% concentration of water soluble polymers in the aqueous phase can enlarge the pore size. In addition, the effect of silica particles, added to the aqueous, and oil phase, on pore size were described. The results showed that in both cases, the pore size of polyHIPEs was extended by increasing amounts of silica loading.

An interesting work was done several years ago and indicated that foam cell sizes were found to be greatly affected by salt concentration. Williams *et al.*, (1990) varied a noninitiator salt, K_2SO_4, at levels from 10^{-6} to 10 $g/100cm^3$ of water and AIBN. The resulting foams showed a 10-fold significantly decrease in cell size at higher salt concentration. Besides, the influence of crosslinking-level was also studied. They varied the amount of DVB from 0%-100%. Up to 10% DVB, the resultant foams were not chalky. Above 20% DVB, they became slightly chalky, and they were very chalky at 100% DVB. The pore size decreased with increaseing in DVB content.

In addition, many studies revealed that ethylene glycol dimethacrylate (EGDMA) as a monomer can generate pores of large size. Livshin *et al.*, (2008) synthesized crystalline polyHIPE based on stearyl acrylate and the relatively flexible EGDMA as a cross-linking comonomer. They then compared it to the relatively rigid divinylbenzene as a cross-linking comonomer, and reported that HIPEs yielded relatively large pores with averages of around 100 μm with increasing EGDMA content. These pores are indicative for destabilization through droplet coalescence and/or Ostwald ripening. However, with increasing droplet size, the distance between them increases as well, resulting in relatively thick walls between the larger droplets. The ability to form interconnected pores decreases as the size of the droplets increases

and therefore, the distance between them, increases. Consequently, the openness and interconnectivity of the porous structure decreased with increasing EGDMA content.

A few years later, this work was supported by Rao *et al.,* (2011). They showed that the water adsorption capacity of novel acrylamide (AAm)–EGDMA polyHIPEs had decreased from 670 to 420% with increasing EGDMA concentration from 30 to 70%, respectively. Theoretically, the swelling of the material is dependent on the nature and concentration of the cross-linking monomer. In this case, the AAm monomer is highly hydrophilic in nature and tends to swell. But, the EGDMA monomer had affected the swelling characteristics of AAm by forming cross-linked networks during polyHIPE formation. Thus, with increasing EGDMA concentration, in the internal phase, the polyHIPE morphology shifted towards a more closed cell structure, resulting in less swelling.

The influence of surface treatment on water adsorption capacity was investigated by Sergienko *et al.*, (2002). They attempted to enhance the hydrophilicity of poly(ethylhexyl acrylate) (PEHA) HIPEs, by two methods: (1) PEHA was first washed in water at 70°C, and then dried; (2) PEHA was immersed into 20 vol % acrylic acid and 0.05 wt % potassium persulphate and cured for acrylic acid polymerization. The results showed that poly(acrylic acid) did not coat the walls, but, rather filled the pores, closing the open-cell structure and reducing porosity. Thus, the poly(acrylic acid) treatment disrupted the open-cell structure and prevented water from penetrating the foam. On the other hand, there was a significant enhancement in PEHA water adsorption following washing in water at 70°C. The water adsorption of PEHA increased from 350% to 500% after washing.