

CHAPTER II

LITERATURE REVIEW

2.1 High Internal-phase Emulsion (HIPE)

A high internal-phase emulsions (HIPE) polymerization process to manufacture microcellular, polymeric foam system was patented by Unilever (Barby *et al.*, 1982). A polyHIPE is a microporous material produced by the polymerization of the monomers in the continuous phase of a HIPE. Microporous foams of very high void fractions (porosities of up to 97%) can be made through polyHIPE synthesis. They are defined as inverse emulsions (water in oil) in which the internal aqueous droplet phase occupies at least 74 vol%. The continuous oil phase consists of monomers (styrene), crosslinking comonomers (divinyl benzene) and nonionic surfactant (sorbitan monooleate) (Walsh *et al.*, 1996). The aqueous phase consists of a water-soluble initiator (potassium peroxydisulfate), stabilizer (calcium chloride hydrate), and deionized water (Tai *et al.*, 2001). Later removal of the water produces a highly open porous polymeric foams, as shown in Fig. 2.1. The foams are open-cell; therefore the large spherical cavities in the material are term cells. The circular hole connecting adjacent cells are referred to as windows. In addition, feature of the morphology such as cell size, interconnecting hole size and porosity can be efficiently controlled.

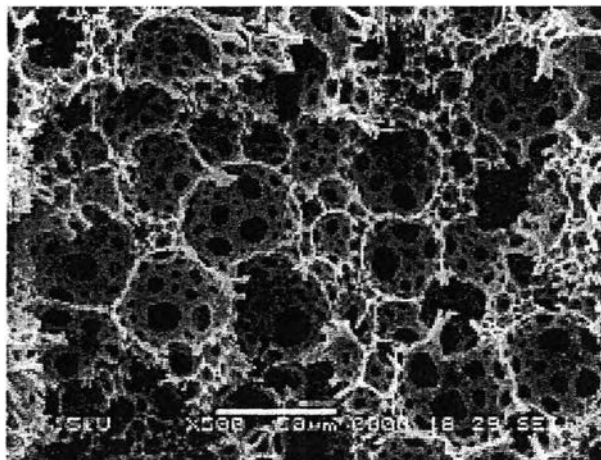


Figure 2.1 SEM of PolyHIPE. (Zhang *et al.*, 2008)

2.1.1 Factor Effective Properties of PolyHIPE

Characteristics of the obtained polyHIPE could be affected by several factors such as addition of porogenic solvents, cross-linking agent, and ratio of mixed surfactants to the monomer phase.

2.1.1.1 *Porogenic Solvent*

Porogen is inert diluents or non-polymerisable solvent such as toluene, chlorobenzene, 2-chloroethylbenzene, and 1-chloro-3-phenyl-propane. The type of porogen added to the continuous phase of polyHIPEs result in the formation of pores within the polymer phase (Barbetta *et al.*, 2004), as shown in Figure 2.2. The walls of the resulting polyHIPE are similar to morphology of permanently porous polymer beads. These may be micro-, meso-, or macropores depend on nature of the porogen.

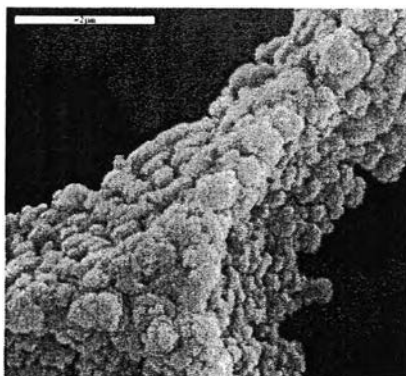


Figure 2.2 SEM of polyHIPE prepared with porogens. (Barbetta *et al.*, 2000)

The nature of the porogen has a strong influence on the surface area, and this is strongly related to the solvent type. Network, or solvent with better solvents for the growing, give rise to higher surface areas (Cameron *et al.*, 1996).

If a good swelling solvent is selected phase separation of the polymer gel phase will be delayed until late in the polymerization. This will produce a large number of small microparticles, which remain discrete until complete conversion is occurred. Since the residual monomer is low, this will result in a material of high surface area. A less efficient swelling solvent, however, causes precipitation of polymer microparticles at an earlier stage when monomer levels are higher. This

residual monomer will locate in the polymer gel phase and cause “filling in” of the gaps between microparticles as it polymerizes. The result is a lower surface area material (Rabelo *et al.*, 1994).

In 2000, Barbeta *et al.* prepared highly porous open-cell polyDVB foams in the presence of various porogenic solvent, either as single components or mixtures, containing toluene (T), chlorobenzene (CB), 2-chloroethylbenzene (CEB), and 1-chloro-3-phenyl-propane (CPP). The nature of the solvent has a profound influence on the foam morphology on both a large and small scale. From SEM, CB was found to reduce the foam cell size (high surface area) compared to T, whereas CEB and CPP seemed to destroy the characteristic PolyHIPE cellular morphology. However from the morphology described above, this material was mechanically very weak and was not likely to be usable in any practical situation. This situation can be remedied by employing mixed porogens. The surface areas of the resulting materials were not predictable in a simple fashion from the values of foams produced from their individual components.

2.1.1.2 Addition of Cross-linking Agent

The employment of an increasing fraction of cross-linking monomer generally leads to porous structures with larger surface areas and smaller pore sizes. The phase separation takes place at a lower monomer conversion for systems with a high fraction of cross-linker (Albright *et al.*, 1986).

In 1990, Williams *et al.* extend their earlier work to include oil phases comprised of 100% styrene or 100% divinylbenzene. In addition, they have studied the influence of degree of crosslinking on the microstructure and compressive properties of the foams. They find that divinylbenzene helps to reduce the cell size. The DVB level has a tremendous effect on cell size. Cells are nonexistent at 100% styrene, are 20-100 μm in diameter with 2.5% DVB present, and are 10-50 μm in diameter at 100% DVB

2.1.1.3 Addition of Mixed Surfactants to the Monomer Phase

The effectiveness of a mixture of an anionic, or a cationic, surfactant with an amphiphilic compound for emulsion stabilization has been known for a long time. The interfacial film made by this mixture of surfactants shows an increased ability to withstand the pressure of droplet contacts (to prevent coalescence)

and to act as a barrier to the passage of the dispersed phase into the continuous phase (to limit Ostwald ripening) (Tadros *et al.*, 1983).

In 2004, Barbetta *et al.* changed the surfactant employed from sorbitan monooleate (SPAN80) to a 3-component mixture of cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (DDBSS) and sorbitan monolaurate (SPAN20) and the result produced some further insights. With this surfactant mixture, surface area values were much higher in almost every case than with SPAN80 (for CB: 689 compared to 346 m² g⁻¹). The improvements were due to the mixtures of ionic and non-ionic surfactants are known to form a more robust interfacial film around each emulsion droplet, leading to enhanced emulsion stability.

In 2006, Sevil *et al.* successfully synthesized polyHIPE by using divinylbenzene and styrene as polymerisable continuous phase, aqueous phase containing potassium persulphate and calcium chloride dihydrate, a mixture of emulsifiers (SPAN20, CTAB and DDBSS) and toluene as a porogen. PolyHIPE samples were found to be porous and open-cell microstructures with the surface area of 370-430 m²/g.

2.2 Application of PolyHIPE

PolyHIPE can be used for many applications, especially as adsorption and filtration medias.

In 1996, Walsh *et al.* illustrated the effect that two properties of the emulsion production process, water to monomer ratio and mixing time, can have on the resultant polyHIPE. It is shown that for an open fibrous type structure the emulsion must have high water content (95%), and that the emulsion must be mixed for a reasonable length of time, in this case of the order of one hour. Such foams have been shown to be very efficient at removing fine particulates from gas flows, with all atmospheric aerosol particles greater than 1 µm diameter being collected.

In 2002, Katsoyiannis *et al.* modified of polymeric materials (polystyrene and polyHIPE) by coating their surface with iron hydroxides in order to remove inorganic arsenic anions from contaminated water sources, among the examined

materials, polyHIPE was found to be more effective in the removal of arsenic, because they were capable in holding much greater amounts of iron hydroxides, due to their porous structure. This enabled the adsorbing agents to penetrate into the interior of the material, which in combination with the surface coating provided a higher surface area available for adsorption.

2.3 Clay Minerals

Clay minerals are hydrous aluminium phyllosilicates, consists of sheets of silica tetrahedral and alumina octahedral which are held together by only weak inter atomic forces between the layers. Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged, these charge are balanced by interlayer cations such as Na^+ or K^+ . In ease the interlayer can also contain water. The crystal structure is formed from a stack of layers interspaced with the interlayers. Clay minerals can be divided into four different groups and these four different groups are kaolite, smectite, illite, and chlorite. Among these, the one that is found to be useful in the field of gas adsorption or gas retention is a group of expandable clay known as smectite clay.

Smectite clay is a group of clay minerals. The smectites are 2:1 layer phyllosilicate constituted of the octahedral sheet containing Al or Mg ions between two tetrahedral silica sheets. There are two different series of smectites: dioctahedral and trioctahedral, according to whether the total number of ions in six-coordination per half-unit-cell layer lies close to 2 or 3, respectively. Montmorillonite, which is the main constitute of bentonites, is a mainly species of smectite clay, as shown in Figure 2.3. These layers organize themselves in a parallel fashion to form stacks with a regular gap between them, called interlayer or gallery. (Manias *et al.*, 2001)

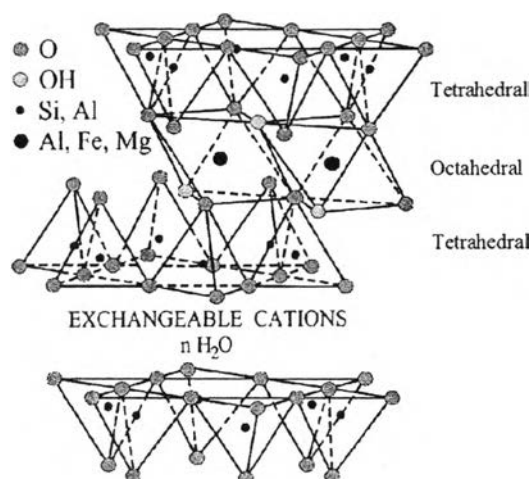


Figure 2.3 Structure of montmorillonite. (Bailey *et al.*, 1980)

The smectites can retain gases but the presence of impurities such as quartz, feldspar, cristobalite, etc. in samples are unfavorable because the adsorption of these minerals is usually small (Volzone *et al.*, 1999; Melnitchenko *et al.*, 2000; Venaruzzo *et al.*, 2002).

Bentonite is clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water. The special properties of bentonite (hydration, swelling, water absorption, viscosity, and thixotropy) make it a valuable material for a wide range of uses and applications.

In 2000, Volzone *et al.* demonstrated that bentonite rich in trioctahedral smectite is a better solid adsorbent than bentonite rich in dioctahedral smectite. Generally, the natural clays have low retention capacity for N_2 , O_2 , CO and CH_4 gases (0.05–0.08 mmol of gas per gram of clay) and a higher capacity for CO_2 , C_2H_2 and SO_2 (0.150–0.636 mmol of gas per gram of clay). Actually, it is possible to mention that the natural smectite as solid adsorbent is better than natural illite and kaolinite (Volzone *et al.*, 2006).

Many of industrial used of smectite clays materials are related to adsorptive capacity which may be increased with acid treatment.

Acid treatment of clay minerals is chemical treatment of the clays to modify structural, textural and/or acidic properties, which influence the adsorption capacity.

composition, charge density, contribute to the adsorption properties. Acid activated clay minerals (by using mainly acid HCl or H₂SO₄ solutions) (Mills *et al.*, 1950) are used as adsorbents and in catalysis because acidic and structural properties are favourable for such applications.

In 1998, Volzone and Ortiga have analysed the retention of CH₄, CO₂, CO, O₂, N₂ and C₂H₂ gases by acid-treated smectites and found that in all cases the acid treatments improved the gas retention with respect to the starting smectites, and the highest adsorption values were found for CO₂ and C₂H₂ gases.

In 2007, Volzone *et al.* treated bentonitic clay minerals with hydrochloric acid at boiling temperature originated an adsorbent with considerable capacities for the adsorption of CO₂, SO₂ gases found that the SO₂ adsorption (up to 1.231 mmol/g) by prepared acid materials were superior to the values of the CO₂ (up to 0.586 mmol/g) and CO (up to 0.119 mmol/g) adsorptions. These effects occur from acid remove the interlayer cation such as Ca²⁺, Na⁺ and K⁺, as well as octahedral cations of the smectite clays in the following order: Mg²⁺>Fe^{2+/3+}>Al³⁺>Ti²⁺ result in increasing surface area due to increase porosity caused mainly by leaching octahedral layer cations of the clay.

In 2008, Pakeyangkoon *et al.* studied the effect of acid-treated clay to CO₂ gas adsorption of polyHIPE by incorporating the acid-treated clay into the monomer phase of the high internal phase emulsion, preparing single surfactant (SPAN80) found that CO₂ gas adsorption capacity increased when acid-treated clay was added.