



CHAPTER II

LITERATURE REVIEW

2.1 High Internal-phase Emulsion (HIPEs)

A high internal-phase emulsion (HIPEs) polymerization process to manufacture microcellular, polymeric foam system was patented by Unilever (Barby *et al.*, 1982). This patent discloses a polymerization process that occurs in a water-in-oil emulsions in which the dispersed phase occupies more than 74% of the volume. The continuous organic phase, which generally constitutes less than 26% of the final volume, can contain monomers (styrene), crosslinking comonomers (divinyl benzene) and organic soluble surfactant (sorbitan monooleate) (Elmes *et al.*, 1988). A poly-HIPE 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 upto 97%) can be made through polyHIPE synthesis. The dispersed aqueous, containing a water-soluble initiator (potassium persulfate) and stabilizer (calcium chloride) (Walsch *et al.*, 1996). Subsequent removal of the aqueous produces a highly porous material, as shown in Fig. 2.1, the obtained 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.

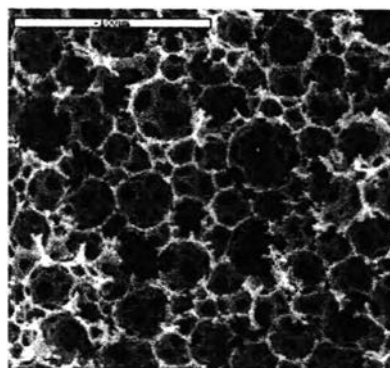


Figure 2.1 SEM of PolyHIPE. (Neil R. Cameron, 2005)

In 1996, Neil R. *et al.* synthesized and characterized of poly(aryl ether sulfone)polyHIPE material. A maleimide-terminated aryl ether sulfone macromonomer was copolymerized with styrene, DVB, in the continuous phase of a HIPE. The cellular structures and porosities of the resulting materials were characterized by SEM, mercury porosimetry, and a Brunauer-Emmett-Teller (BET) treatment of nitrogen adsorption results. All were shown to possess an open-cellular morphology and a secondary pore structure within the polymer walls. Thermogravimetric analysis (TGA) of the materials indicated that critical degradation occurred at higher temperatures than in poly(styrene/DVB) polyHIPE.

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.

In 2008, Pakeyangkoon *et al.* studied the effects of organo-clay on poly(DVB)HIPE. They found that the surface properties enhancement poly(DVB)HIPE was due to the incorporation of layered silicates into polyHIPE matrix and the maximum improvement of mechanical properties (compressive stress and Young's modulus) was observed when 5 wt% of organoclay was added into the polyHIPE system (Figure 2.2).

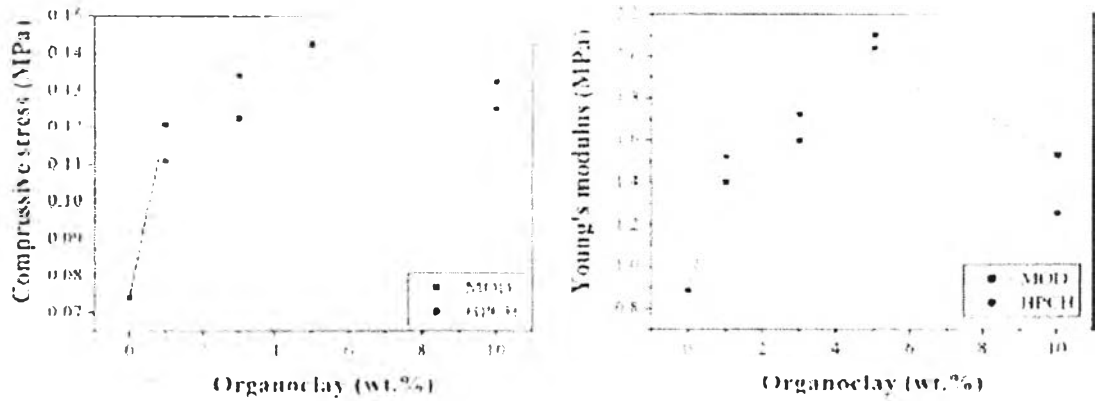


Figure 2.2 Compressive stress and Young's modulus of poly(DVB)HIPE filled with organo clay.

In 2009, Pannak *et al.* tried to improve the mechanical properties and increase the adsorptive capacity of poly(DVB)HIPE by adding acid treated clay. They found that CO₂ adsorptive capacity depended on type of clay and surface area of poly(DVB)HIPE. A large specific surface area was preferable for providing a large adsorptive capacity (Figure2.3).

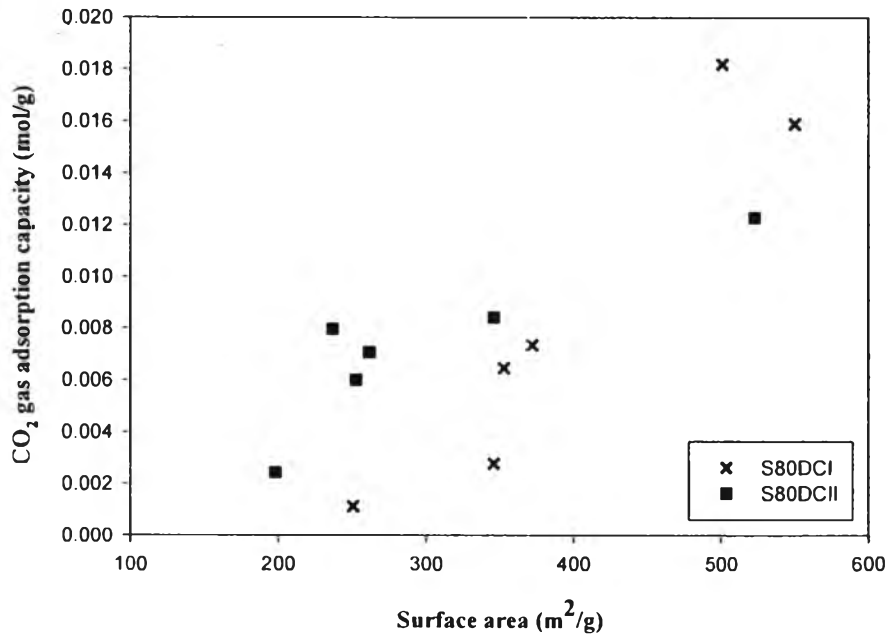


Figure 2.3 Surface area and adsorptive capacity of poly(DVB)HIPE filled with acid treated clay.

2.1.1 Application of PolyHIPE

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

In 1996, Walsh *et al.* illustrated that the effect of two properties of the emulsion production process, water to monomer ratio and mixing time, can have on the resultant polyHIPE. It was 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, Ioannis *et al.* modified 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 of 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.

2.2 Polysulfone

Polysulfone describes a family of thermoplastic polymers. These polymers are known for their toughness and stability at high temperatures. They contain the sub-unit aryl-SO₂-aryl, the defining feature of which is the sulfone group. Polysulfones were introduced in 1965 by Union Carbide. Due to the high cost of raw materials and processing, polysulfones are used in specialty applications and often are a superior replacement for polycarbonates.

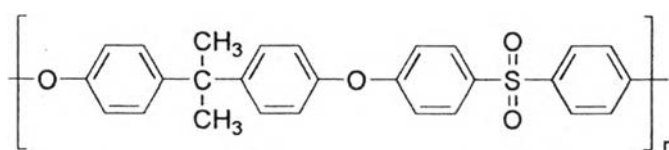
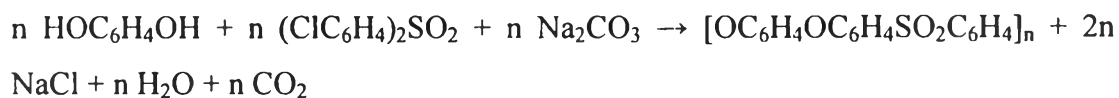


Figure 2.4 Polysulfone repeating unit

2.2.1 Production of Polysulfone

A typical polysulfone is produced by the reaction of a diphenol and bis(4-chlorophenyl)sulfone, forming a polyether by elimination of sodium chloride:



The diphenol is typically bisphenol-A or, as shown above, 1,4-dihydroxybenzene. In 2002, Parker *et al.* studied such step polymerizations require highly pure monomer to ensure high molecular weight products.

In 1991, Jin and Yee used bisphenol A to construct maleimide-terminated poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene). These oligomers (sulfone) were easy to process and cure.

2.2.2 Chemical and Physical Properties of Polysulfone

Polysulfone is a rigid, high-strength, and transparent, retaining its properties between $-100\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$. It has very high dimensional stability; the size change when exposed to boiling water or $150\text{ }^\circ\text{C}$ air or steam generally falls below 0.1%. Its glass transition temperature is $185\text{ }^\circ\text{C}$.

Polysulfone is highly resistant to mineral acids, alkali, and electrolytes, in pH ranging from 2 to 13. It is resistant to oxidizing agents, therefore it can be cleaned by bleaches. It is also resistant to surfactants and hydrocarbon oils. It is not resistant to low-polar organic solvents (eg. ketones and chlorinated hydrocarbons), and aromatic hydrocarbons. Mechanically, polysulfone has high compaction resistance, recommending its use under high pressures. It is also stable in aqueous acids and bases and many non-polar solvents; however it is soluble in dichloromethane and methylpyrrolidone.

In 2001, Reid *et al.* studied gas permeability properties of polysulfone membranes and enhanced the gas permeability characteristics of a high-performance polysulfone with additive (MCM-41). They found that polysulfone is more selective, especially carbondioxide (CO_2) which have the highest value from the table. (see Table 2.2)

Table 2.1 Permeabilities (Barriers) of various gases in PSF and MCM-41/PSF composite membranes

membrane	MCM-41 % (w/w)	O ₂	N ₂	CO ₂	CH ₄
PSF	0	1.50 ± 0.07 ^a (3) ^b	0.257 ± 0.036 (2)	7.53 ± 2.07 (2)	0.389 ± 0.008 (2)
PSF ^c	0	1.4	0.25	5.6	0.26
MCM-41:PSF	10	1.79 ± 0.10 (6)	0.354 ± 0.010 (5)	10.5 ± 0.9 (2)	0.586 (1)
MCM-41:PSF	20	2.16 ± 0.01 (10)	0.395 ± 0.014 (5)	11.4 ± 1.8 (2)	0.603 (1)
MCM-41:PSF	30	3.83 ± 0.02 (3)	0.753 ± 0.11 (4)	20.5 ± 0.9 (2)	1.05 ± 0.09 (2)
silica:PSF	10% silica	1.36 ± 0.14 (3)	0.23 ± 0.05 (3)	7.72 ± 0.9 (3)	0.16 ± 0.08 (3)

^a 95% confidence limits. ^b () number of runs. ^c Reference 16.

2.2.3 Applications of Polysulfone

Polysulfone is used as a dielectric in capacitors. Polysulfone allows easy manufacturing of membranes, with reproducible properties and controllable size of pores. Such membranes can be used in applications like hemodialysis, waste water recovery, food and beverage processing, and gas separation. These polymers are also used in the automotive and electronic industries.

Polysulfone can be reinforced with glass fibers. The resulting composite material has twice the tensile strength and three time increase of its modulus.

Polysulfone has the highest service temperature of all melt-processable thermoplastics. Its resistance to high temperatures gives it a role of a flame retardant, without compromising its strength that usually results from addition of flame retardants. Its high hydrolysis stability allows its use in medical applications requiring autoclave and steam sterilization. However, it has low resistance to some solvents and undergoes weathering; this weathering instability can be offset by adding other materials into the polymer.

It is supplied by Solvay Advanced Polymers, BASF, HOS-Technik and PolyOne Corporation. Polysulfone is also used as a copolymer.

2.3 Gasification Process

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, or biomass, into carbon monoxide, carbon dioxide, and hydrogen by reacting the raw material at temperatures above 700°C when the carbonaceous materials are allowed to react with a gasification agent such as oxygen, air, or steam.

Air is one of the main basic elements of life. Air pollution implies the presence of harmful substances in the air (nitrogen oxides, particulate matter, sulphur dioxide, hydrocarbons, carbon monoxide, ozone, etc.). These substances needless to say cause bad serious effects on our health. Adsorption processes have become useful tools to remove pollutants by using mainly carbon (Kapoor *et al.*, 1989), zeolites (Jun *et al.*, 2002) and modified silica materials (Huang *et al.*, 2003)

In 2001, Zou Yong *et al.* studied the adsorption capacity of carbon dioxide on high surface area carbon-based adsorbents before and after chemical modification at 28°C and 300°C found that the high adsorption capacity adsorbents for carbon dioxide at high temperature have been developed by introducing MgO and S-CaO-MgO on carbon-based adsorbents. Their adsorption capacities for carbon dioxide were 0.28 and 0.22 mmol/g at 300°C, 1 Bar, respectively.

In 2002, Jun *et al.* showed the zeolite adsorbents used for the gas adsorption processes. Especially, as the ratio of SiO₂/Al₂O₃ increases, the adsorbed amount of moisture is reduced while the adsorbed amounts of strong adsorbates like acid gases are little reduced. As a result, the selective adsorption of acid gases coexisting together with moisture becomes possible. It is known that the adsorbing performance of zeolite is remarkably deteriorated because Al in the network of Si-O-Al constituting the crystal structure reacts with acid gases absorbed on zeolite and it is released from the crystal lattice.

In 2005, Lidia studied influence of method and conditions of spent Pd/Activated Carbons catalyst regeneration on its catalytic activity. It has been stated that supercritical fluid extraction (CO₂) followed by heating in hydrogen atmosphere is an effective method of that catalyst regeneration. The results of FTIR and XPS investigations indicate that regeneration of a spent Pd/Activated Carbons catalyst, irrespective of the reaction in which it has been used, should be based on the complete

removal of by-products and cleaning the catalyst surface as well as on restoring the original form of the palladium.