CHAPTER I
INTRODUCTION

Polymerization of high internal phase emulsion (HIPE) is a method to produce highly open porous polymeric foam with interconnecting pore networks (Barby *et al.,* 1982; Williams *et al.*, 1988; Hainey *et al.*, 1991). This porous material so called polyHIPE porous foam which has been defined as emulsions where the internal phase occupies more than 74% of the total volume. The continuous organic phase, which generally constitutes less than 26% of the final volume, can contain monomers, crosslinking comonomers and organic soluble surfactant (Elmes *et al.*, 1988). The outstanding characteristics of polyHIPE porous foams are its three-dimensional structure, as well as the highly porous materials with interconnected pores and very low density. These characteristics make polyHIPE porous materials being considered attractive for many applications, such as selective adsorbent, ion exchange membrane, and scaffold for tissue engineering applications (Wakeman *et al.*, 1998; Akay *et al.,* 2004). Unfortunately, polyHIPE porous foam has low crush strength, chalkiness and brittleness, poor mechanical performance of polyHIPE foam was also obtained leading to limits their practical use in most industrial applications. Morever, in case of tissue enginnering applications, polyHIPE foam scaffold synthesized via HIPE technique have been made of hydrophobic polymers such as polystyrene (PS), which is improper for supporting the cell–scaffold interaction, poor interaction and adhesion between scaffold and living could be obtained (Ryu *et al.*, 2005; Lee *et al.*, 2008). Thus, the key purpose of this research work was focused on the methods for modification of polyHIPE foam performance for using in two main applications including adsorbent for CO_2 adsorption and scaffold for tissue engineering applications through using three-component surfactant systems, Soxhlet extraction technique, adding inorganic filler, and using plasma surface modification.

Air pollution is one of the most important environmental problem today, which is caused by many different sources. Air pollution is any chemicals or compounds, consist of carbon monoxide (CO), sulfur dioxide (SO_2), volatile organic compounds (VOCs), lead and carbon dioxide (CO_2), which the major sources come from both natural and manmade. Especially, the mainly cause is the industrial activities, which is carried out by human. Carbon dioxide (CO_2) is one of the major pollutants in the atmosphere, which is toxic to the body and can result in breathing and other health problems (Volzone *et al.*, 2007). Moreover, the formation of huge volume of CO_2 which contributes to the creation of the greenhouse effect is presented in the atmosphere like pollutants (Bodzek, 2000). To minimize this problem, it is very important to design adsorbent materials that would adsorb such gases before being liberated into the environment. Many scientists developed the adsorbent for gas adsorption in air treatment process i.e. by using zeolites and/or silica as solid adsorbent in gas separation process (Yang *et al.*, 1987; Kapoor *et al.*, 1989). In 2007, Volzone *et al.* reviewed that clay mineral and their modified products i.e. organo-modified clay and acid treated organo-modified clay can be used as solid adsorbents in gas adsorption technology, which help us to remove as much as greenhouse gases emission and pollutants to the atmosphere (Volzone *et al.*, 2007).

PolyHIPE porous foams is also a polymeric foam being considered as an adsorbent material for adsorption of toxic gases in air treatment process. This is because of its high porosity with interconnected pore structure of polyHIPE material and also the ease of fabrication and regeneration make it ideal candidate to be used in the adsorption process. Results from the literature survey have demonstrated that one of the most important requirements for the success of polyHIPE in applications is its high surface area and high porosity with small cell size and interconnectivity. Presently, there are many work attempting to further improve the surface properties of polyHIPE materials. Usage of the three-component surfactants with inert porogenic solvent increase the emulsion stability of the system and high surface properties of the polyHIPE can be obtained when a secondary pore structure is generated within the cell walls of the obtained materials (Barbetta *et al.*, 2004; Cameron *et al.*, 2005). In addition, polyHIPE morphology was found to be affected by the nature of surfactant used in the preparation (Williams *et al.*, 1991). They reported that Span80, a surfactant with hydrophilic-lipophilic balance (HLB) 4.3, could act as the most suitable surfactant to produce stable emulsion for poly(S/DVB)polyHIPE system. As part of our work, nature of surfactant on the characteristic of polyHIPE foam was studied. PolyHIPE materials containing divinylbenzene were synthesized by using three different systems of surfactant including S80 (single surfactant), S80M and S20M (mixed surfactant; three-component surfactants) in order to investigate the effect of different systems of mixed surfactant.

Generally, polyHIPE polymer with closed cell type will be formed because of rest monomers, residual surfactants, and porogenic solvent in the continuous phase are trapped within the cellular structure of polyHIPE porous polymer. This leads to produce polyHIPE materials with low surface properties. To overcome this problem, the Soxhlet extraction technique is needed to remove the residual materials from pore structure of polyHIPE foam and the resulting materials with high surface properties would be obtained. Additionally, the effects of Soxhlet extraction time on the resulting materials was investigated by Alexander and co worker. They showed that the extraction times were found to have an effect on the mechanical and flammability properties of the resulting polypropylene nanocomposite (Alexander *et al.*, 2003). From this observation, the optimum Soxhlet extraction time, to achieve the good properties (both surface area and mechanical properties) of poly(DVB)polyHIPE foam, was also investigated in this study.

Not only is high surface area an important requirement for polyHIPE foam to be practical in industrial applications, good mechanical properties are also equally important. More researchers were focused on ways to improve the physical properties of polyHIPE foam using inorganic materials i.e. silica and carbon black as a reinforcing agent (Haibach *et al.*, 2006; Menner *et al.*, 2006). In a number of investigations, modified clay mineral was found to significantly affect the overall properties of the polymeric composite materials. Modifying clay mineral using ion exchange reaction with quaternary ammonium cations, will result in layered silicates in clay being expanded and the d-spacing of organo-modified clay is increased. After modification, organo-modified clay can be compatible with polymer matrix and play an important role as an inorganic reinforcement (Fornes *et al.*, 2004). The introduction of few percentages of organoclay into polymer matrix is well-known to result in significant improvement in mechanical strength due to nanometric dimensions and high aspect ratio of the clay mineral (Jo *et al.*, 2007). Moreover, there are reportes that clay mineral would not only provide reinforcement but also adding new properties. Clay mineral and their modified products i.e. porous clay, organo-modified clay, and acid treated clay are recognized as potential adsorbents. The incorporation of layered silicate in the polymer matrix should lead to improving the surface properties, thermal stability and gas adsorption capactity, of the obtained materials as well (Pakeyangkoon *et al.*, 2009). This is because of the increasing of d-spacing of organo-modified clay by using ion exchange reaction which can also improve the capability of organo-modified clay itself for adsorption of gas molecule into the layered silicates whereas inherent characteristics of porous clay, which exhibited open-framework of silica and high surface area with uniform pore diameter in the clay galleries. In addition, researchers attempted to increase adsorptive capacity of organo-modified clay with using acid treatment. The octahedral ions are leached out, resulting in better improving the surface area and gas adsorption capacity of the organo-modified clay after acid treatment (Volzone *et al.*, 2000; Volzone *et al.*, 2002; Venaruzzo *et al.*, 2002; Volzone *et al.*, 2006). Then the major aim of this part was to enhance surface area, mechanical properties and also CO_2 adsorption capacity of polyHIPE foam by using three types of organoclay as inorganic filler for poly(DVB)polyHIPE porous foam, including hybrid organic-inorganic porous clay heterostructure (HPCH), organo-modified bentonite (MOD), and acid treated organo-modified bentonite (AC-MOD).

Three dimensional highly open porous polymeric foam, produced from a high internal phase emulsion (HIPE) technique is one of the most widely used synthetic materials in tissue engineering application (Akay *et al.*, 2004; Hayman *et al.*, 2005). Poly(Styrene/Divinylbenzene)polyHIPE foam has successfully been tested for its ability to support the growth of cells, and it has good biocompatibility between osteoblasts and solid supports in the *in vitro* environment (Akay *et al.*, 2004). Moreover, biomaterials based polyHIPE foam i.e. poly(ε-caprolactam; PCL) and polylactic acid (PLA) have been investigated (Busby *et al.*, 2001). These biomaterials are sufficiently biocompatible to support cell function and growth into polyHIPE substrate. Additionally, there are many reports indicating that ethylene glycol dimethacrylate (EGDMA) monomer and its derivative have been widely used in the fabrication of substrate for scaffolds in tissue engineering applications because substrate materials prepared from EGDMA could be provide good biocompatible, high water uptake, and have relatively low cytotoxicity (Gibson *et al.*, 2005). Thus, poly(styrene/ ethylene glycol dimethacrylate)polyHIPE foam scaffold was successfully prepared in this part of works in order to study the interaction between polyHIPE substrate and living cell. However, polyHIPE scaffolds based on polystyrene (PS), which by nature has hydrophobic characteristics could not improper for supporting the cell–scaffold interaction, and poor adhesion between cell and substrate is obtained. Therefore, it is difficult for the culture media to penetrate the porous scaffold structure throughout and attach to the polyHIPE surface, consequently not promoting cell spreading, seeding, and growth. So, the modification of polyHIPE substrate is a must in order to produce suitable materials for tissue engineering applications and the most interest one is in plasma surface modification. Surface of substrate materials with using plasma surface modification were modified and increased hydrophilic characteristic for example surface of poly(D,L-lactid-co-glycolic acid)—PLGA— and PCL film was modified by using plasma technique lead to enhance the cell attachment and proliferation (Ryu *et al.*, 2005; Lee *et al.*, 2008) Thus, another aim of this research work was played an attention on the improvement of polyHIPE scaffold/cell interaction for tissue engineering applications using surface modification technique via atmospheric pressure plasma treatment. The amount of cell adhesion and proliferation of poly(S/EGDMA)polyHIPE scaffold with and without plasma surface modification was examined in this study.