CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 CO_2 Separation Techniques

In a field of separation of CO_2, most common techniques used can be applied for capture of CO_2 regarding to mitigation of greenhouse gases. The techniques are: (i) absorption, (ii) adsorption, (iii) gas separation membrane and (iv) cryogenic distillation. Among these techniques, absorption and adsorption are mostly used.

2.2 Absorption

Absorption is a physical or chemical process in which chemical species are dissolved in a bulk phase. It is a common process for treating gas stream in the post combustion systems with absorbent molecule containing functional group, such as, hydroxyl (-OH) or amino ($-NH_2$, -NHR, and $-NR_2$) groups. At the presence, amines, such as monoethanolamine (MEA) is widely used for CO_2 absorption. However, there are some drawbacks about corrosion that affect to equipment in the process and the amine degradation.

In 2010, Freeman *et al.* studied CO_2 capture using concentrated aqueous piperazine and achieved fast kinetics and low degradation rates when compared with MEA process.

In 2001, Mandal *et al.* improved a rate of absorption of CO_2 using amine compounds mixture. Absorption rates of MEA/MDEA and MEA/AMP mixtures were higher than pure MDEA and AMP.

2.3 Adsorption

Adsorption is also considered as an alternative process for CO_2 capture. It is a selective process which adsorbate molecules in a liquid or gaseous phase are adsorbed on a solid surface of adsorbent. A main factor which can affect adsorption ability is surface area. The higher surface area, the more opportunity to capture CO_2 a adsorbent has It is known that the adsorption is an exothermic process and the regeneration of the adsorbents through desorption can be performed by raising the temperature (Pires, 2011).

There are some advantages of adsorption process (Damen *et al.*, 2006b), i.e. the reaction may be performed in a single reactor, which reduces capital costs, the reduction of steam needed in the reaction. the process captures CO_2, which is environmentally friendly and may eliminate the need for a dedicated CO_2 capture unit

An adsorption process can be classified into two types according to a way in which the adsorbent is changed between the adsorption and desorption steps. i.e. changing in pressure (called pressure swing adsorption, PSA) or in temperature (called temperature swing adsorption, TSA).

In pressure swing adsorption (PSA). adsorption and desorption process occurs by changing the pressure. the pressure is increase in the adsorption step, on the other hand, pressure is decrease in the desorption step. The higher the pressure, the more gas is adsorbed. In temperature swing adsorption (TSA). adsorption step will occur in a range of low temperature. When the temperature increases, the desorption step will take place. In general, adsorbents used are porous materials, such as zeolite, activated carbon, silica gel and also metalloid material like alumina.

There are wide applications of adsorption, such as in the production of ammonia, removing of hydrogen sulfide. and also in carbon dioxide removal. The adsorption techniques can be an alternative technique of choices. However, adsorption capacity and CO_2 selectivity of adsorbents for CO_2 capture have to be high.

2.4 Properties of Adsorbent

In order to use adsorbents for adsorption, the adsorbents, in general, should have properties, such as high adsorption capacity with adsorbate molecules, suitable chemical structure, high surface area, good thermal stability, good mechanical property, and also porosity and pore size distribution for separation or molecular sieve process. In the term of selectivity, chemical structure of adsorbents, are considered important, for example, an adsorbent functionalized with amine for CO_2 capture. In the context of contacting between adsorbate and adsorbent, surface area is the one of important factor, which effects on quantity and rate of adsorption directly. The higher surface area, the more opportunity of adsorbent adsorbs the adsorbates. In order to prolong life time of adsorbents, operating temperature of adsorbents is considered. For high operating temperature, it requires the adsorbents to have high thermal stability. Moreover, mechanical property is also, related to the life time of adsorbents.

## 2.5 High internal phase emulsion polymerization (PolyHIPE)

Polymer obtained by polymerization in high internal phase emulsion (HIPE) called polyHIPE is material containing very high porosity and high surface area in which internal phase volume can be greater than 74.05 %vol. It is used in a wide range of applications in food, cosmetic, pharmaceutical, and petroleum industries. The preparation of poly HIPE can be divided into two types, which are oil-in-water (oil dispersed in water) and water-in-oil (water dispersed in oil) emulsions. The main ingredients of polyHIPE are monomer, cross-linker, surfactant, initiator, poragen and stabilizer. A function of stabilizer is to stabilize the emulsion. Surfactant is generally used to stabilize the emulsion by balancing the hydrophilic part and hydrophobic part. PolyHIPE is one of candidate material which may be suitable for use as adsorbent. It can be designed by selecting types of monomer suit to applications. Generally, non-polar compounds are used, such as styrene, divinylbenzene (DVB), and vinylbenzylchloride (VCB) as a monomer in a continuous oil phase, on the other hand polar compounds can be used, such as methyl methacrylate (MMA).

When the PolyHIPE is synthesized, its surface can be modified by various compounds, for example, polyHIPE containing chloride group in the structure as shown in Figure 2.1. Pathway numbers 2 and 5 are of interest, which can be functionalized to products containing the amine group which has potentials to adsorb CO_2. (Carmeron, 2005).
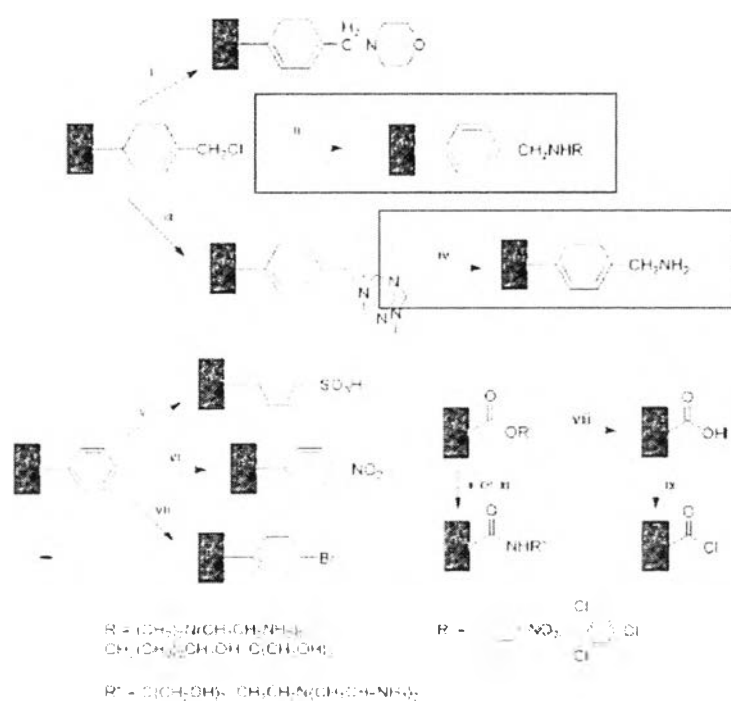
Figure 2.1 Functionalization of polyHIPE materials (Carmeron, 2005).

In general, the surface properties depend on pore size, pore diameter, surface area, and also functional group of surface structure. Gray et al. (2004) modified fly ash carbon sorbents with amine compounds for CO_2 adsorption. 3-Chloropropylamine-hydrochloride (CPAHCL) and amine modifier were used to modify the hydroxide or carboxyl group on the surface of fly ash to obtain the amine-enriched fly ash carbon sorbents as shown in Figure 2.2.
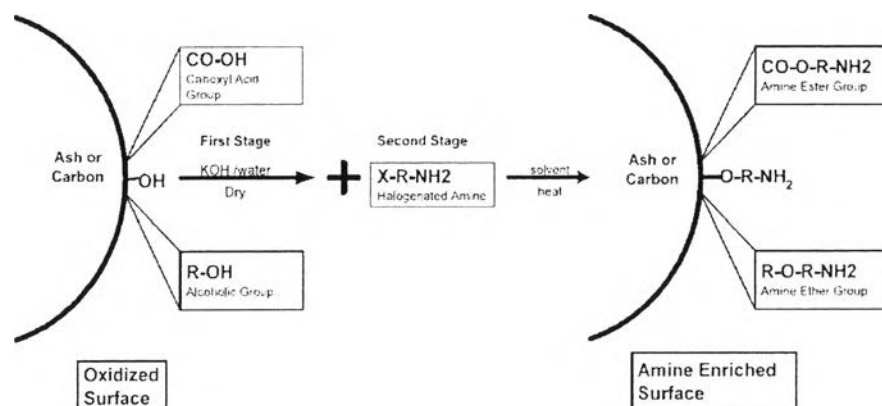
Figure 2.2 Modification of fly ash carbon adsorbent surface (Gray *et al.*, 2004).

The properties of modified sorbent were characterized by infrared transform spectroscopy (DRIFTS), temperature programmed desorption (TPD), mass spectroscopy (MS), and the amount of nitrogen on the surface of the amine - enriched fly ash carbon sorbent by X-ray photoelectron spectroscopy (XPS). The CO_2 adsorption and CO_2 desorption of adsorbent treated with CPAHCL gave highest results of 174.6μmol/g sample.

A crosslinked structure of polyHIPE is a result of diene monomer, which can crosslink and the degree of crosslinking affect to polyHIPE stability at high temperature. Generally, materials containing crosslinked structure, they will not melt, but decompose at higher temperature (Odian 2004).

Hoisington and co-workers (1997) prepared polyHIPE using styrene, divinylbenzene (DVB), N-ethylmaleimide and/or bismaleimide (BMI) as monomers by water-in-oil emulsion. This research was focused on effect of composition of monomers on the thermal properties of polyHIPE, glass transition temperature (T_g) and decomposition temperature, because T_g of the conventional styrene/divinylbenzene foam is low approximately 100°C. The dynamic mechanical analysis (DMA) was used to evaluate T_g of the formed samples. The temperature increased from around 125°C (conventional form) to higher temperature with increasing the quantity of ethylmaleimide due to ethylmaleimide penetrating into the polystyrene chains during the crosslinking and creating large blocks of styrene.Thermogravimetric analysis was used to examine thermal stability behaviour.

When the amount of ethylmaleimide in polyHIPE was increased, the thermal stability was also increased. Moreover, the mechanical properties of polyHIPE such as density, compression strength, and specific compression were increase with increasing ethylmaleimide and/or bismaleimide (BMI). The mechanical properties of polyHIPE containg only ethylmaleimide was greater than that of polyHIPE containing both ethylmaleimide and BMI due to more uniform open cell structure than the latter structures that were observed by scanning electron microscopy (SEM).

2.6 Emulsion Polymerization (Odian, 2004)

Emulsion polymerization was first used during World War II for producing synthetic rubber. The main components are monomer, dispersing medium, emulsifier, and water-soluble initiator. Generally the dispersing medium is water. The emulsifier is so called surfactant due to its structure having both hydrophilic and hydrophobic segments. Smith and Ewart (1948) and Harkins (1947) explain the distinct features of emulsion polymerization based on their studies of polystyrene, which can be divided into three stages or intervals as shown in Figure 2.3.

Interval I

Monomers (organic or oil phase) are dispersed in the aqueous solution containing initiators, surfactants and water. Micelle is a surfactant aggregate which its concentration is greater than the critical micelle concentration (CMC). The polymerization process occurs by reactions of initiators with monomers in the micelles to get the oligomer radicals which continue to propagate by reacting with the monomer in the micelles until becomes the polymer chains called latex. When micelles growing by aggregation of micelle, the amount of surfactants adsorbed on the surface of micelles is not enough to stabilize, the surface tension of solution is increased dramatically. This interval ends immediately after the exhaustion of micelles.
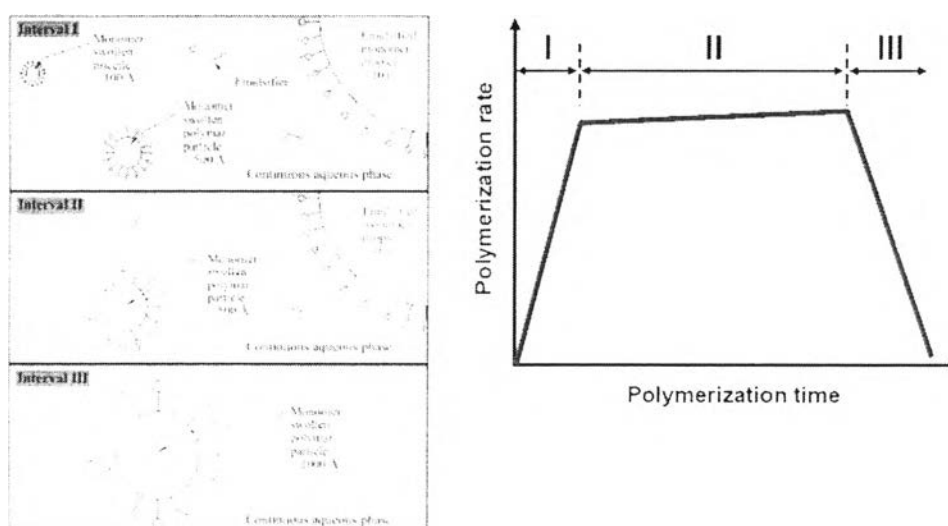
Interval II

After the interval I completed, the new polymer chains cannot occur in this interval due to depletion of micelles. Most of emulsifier was used to stabilize in the interval I, but the polymerization reaction still going. Therefore, the size of polymer

particles growing steadily, called polymer particle. The decrease of amount of the monomer in micelle causes the rate of polymerization slowly increase, which results in Trommsdorf effect or auto-acceleration to appear due to the localized increase of viscosity of the polymerizing system that slows the termination reactions.

Interval III

The reactions in the polymer particles are going until all of monomers in the system are polymerized. Therefore, polymerization rate is decreased with time.

Figure 2.3 Step of emulsion polymerization: interval I-III and rate of polymerization (Kim, 2007).

Advantages of emulsion polymerization (Odian, 2004)

- The emulsion polymerization can make high molecular weight polymers with fast polymerization rates. On the contrary, in bulk and solution free radical polymerization, it inverses variation between molecular weight and polymerization rate.

- The continuous water phase of emulsion polymerization is an excellent conductor of heat, which allows the heat to be removed from the system and many reaction methods to increase their rates. On the contrary bulk polymerization is occurred without water phase, so it creates a large quantity of heat and limit polymerization rate.

- The emulsion polymerization viscosity is not dependent on molecular weight of polymer because polymer molecules are contained within polymer particles, on the other hand, other types of polymerization viscosity is increased with molecular weight.

- The final product can be used directly.

Disadvantages of emulsion polymerization (Odian, 2004)

- Surfactants and other polymerization adjuvant remain in the polymer or are difficult to remove.

- For dry polymers, water removal is an energy-intensive process.

- Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.

- Cannot be used for condensation (polymerization that occur via condensation reaction), ionic polymerization (forming by cationic or anionic monomer) or Ziegler-Natta polymerization (that is used Ziegler-Natta catalyst as initiator), although some exceptions are known.

2.7 Preparation of PolyHIPE

PolyHIPE is prepared by radical polymerization in emulsion. The emulsion polymerization process has several advantages, such as it easy to control and there are fewer problems from processing temperature and viscosity than in bulk polymerization. The product called latex can be used directly without separation, such as pigment and glue.
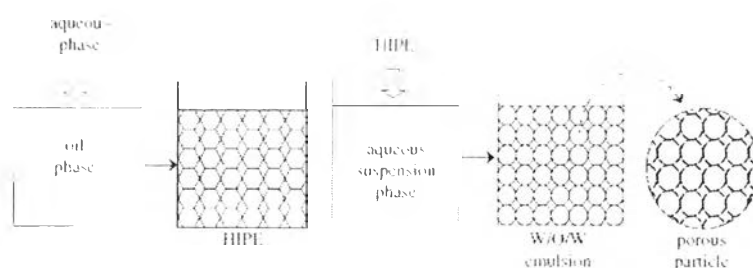
2.7.1 Preparation

Li and Benson (1996) patented a method for the preparation of polyHIPE beads of styrene-DVB polymer using water-in-oil high internal phase emulsion of which oil droplets were dispersed in the water and then polymerized. Resulting polymer particles were beads with open cellular structure, very similar to that known monolithic. On the other hand, polyHIPE materials can be prepared from oil-in-water emulsions (Zhang and Cooper, 2002). Hydrophobic organic liquids, such

as paraffin can be emulsified in an aqueous solution of hydrophilic monomer plus crosslink agent.

Stefanec and Krajnc (2005) investigated vinylbenzyl chloride based porous spherical polymer supports derived from water-in-oil-in-water emulsions (W/O/W). Firstly, polyHIPE was synthesized by W/O emulsion using DVB and VBC as monomers with high fraction of VBC in order to raise up the quantity of chloride functional group that can be modified by amine compounds. To form porous bead the PolyHIPE was suspended in an aqueous phase of poly(N-vinylpyrrolidone) (PVP) as shown in Figure 2.4. Finally, the surface of the porous particles was modified by amine compounds as shown in Figure 2.5. The average diameters of the bead particles were found to increase with decreasing the content of PVP. The characterization of chemical structure by Fourier transform infrared spectroscopy (FTIR) after functionalized with amine found that peak of C-Cl bond disappeared, which confirmed the loss of chloride group of VBC, and peaks of -NH and -OH strongly appeared. Moreover the result of CHN element analysis for degrees of conversion found that all cases have high degrees of conversion between 54 % - 84 %.


Figure 2.4 Preparation of porous beads by polymerization of W/O/W emulsion (Stefanec and Krajnc, 2005).
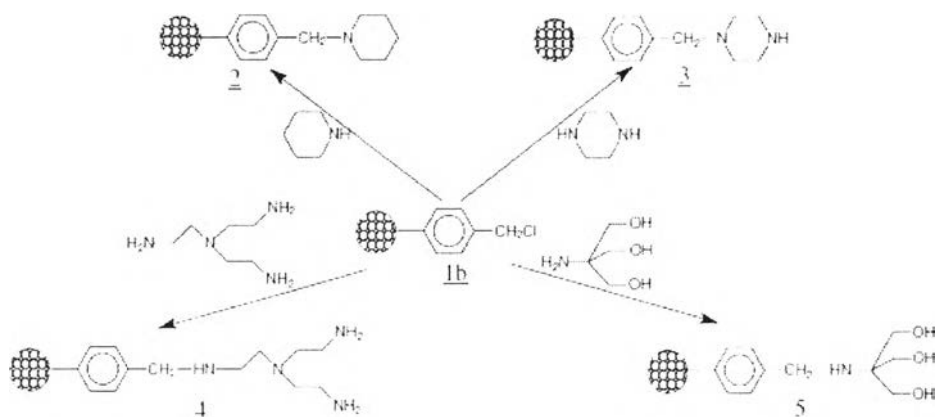
Figure 2.5 Functionalization of VBC/DVB porous particles (Stefanec and Krajnc, 2005).

Zhang and Cooper (2002) synthesized monodisperse emulsion-templated polymer beads by oil-in-water-in-oil (O/W/O) sedimentation polymerization. Light mineral oil (LMO) was used as disperse oil phase. Acrylamide (AM) and N,N-methylenebisacrylamide (MBAM) as monomer in continuous aqueous phase. First, the oil-in-water HIPE was formed by slowly adding LMO to the aqueous solution of monomer. The polymerization occurred when adding ammonium persulfate (initiator), which resulted in a stable O/W HIPE formation. This HIPE was injected into a glass column containing LMO to form the droplets. The final results were beads with large macropores (2-15μm) and high pore volumes as shown in Figures 2.6 and 2.7.
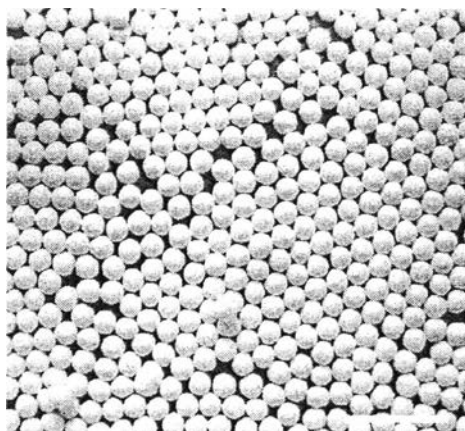
Figure 2.6 Optical image of emulsion-templated beads (Zhang and Cooper, 2002).
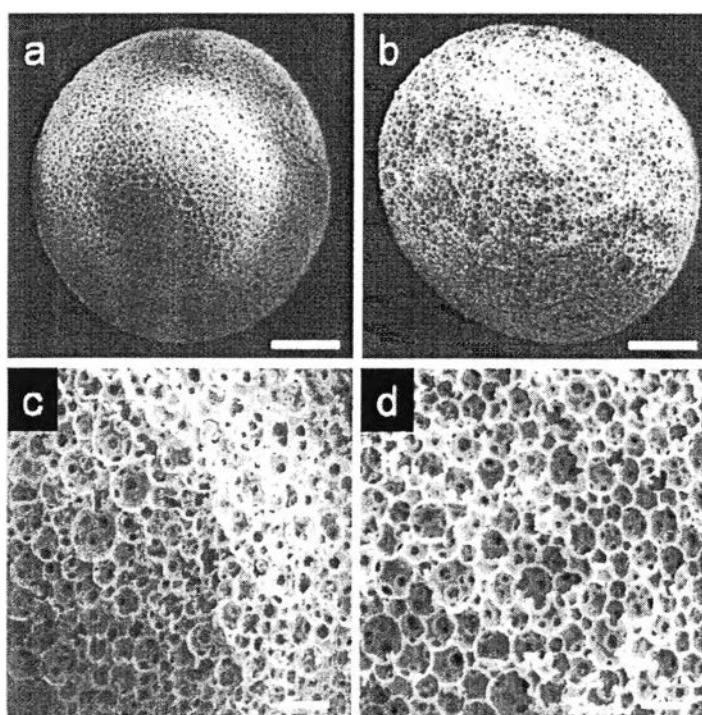
Figure 2.7 Electron micrographs of individual emulsion-templated beads (a) whole bead (scale bar =500μm). (b) Selected half-bead showing internal pore structure (scale bar =500μm). (c) Magnified image of bead surface (scale bar =100μm). (d) Magnified image of a fracture in a sectioned bead showing internal pore structure (scale bar =100μm) (Zhang and Cooper, 2002).

2.7.2 Effect of surfactant

Zhang *et al.* (2011) prepared polyHIPEs without using surfactant, but poly styrene-methyl methacrylate-acrylic acid (P(St-MMA-AA)) copolymer particles as a stabilizer instead of surfactant. P(St-MMA-AA) was tested in both organic phase (series A) and in aqueous phase (series B) before emulsification. When the copolymer particles was in the organic phase (series A), the average void diameter decreased with increasing the copolymer concentration due to the increases viscosity of the external phase of W/O HIPE, hence improves the stability of emulsion. As the result, the average droplet diameter decrease and consequently decrease the average void diameter. When the copolymer particle was in aqueous phase (series B), the void diameter is decreased with increasing the copolymer particles concentration due to close packed particles as observed by SEM.

Hydrophilic-lipophilic balance (HLB) of a surfactant is a measure of the degree of hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule, as described by Griffin (1949). An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 corresponds to a molecule made up completely of hydrophilic components. The HLB value can be used as an initial guide to select the surfactant for applications.

- A value < 10 : Lipid soluble (water insoluble)
- A value > 10 : Water soluble
- A value from 4 to 8 indicates an anti-foaming agent
- A value from 7 to 11 indicates a W/O (water in oil) emulsifier
- A value from 12 to 16 indicates an O/W (oil in water) emulsifier
- A value from 11 to 14 indicates a wetting agent
- A value from 12 to 15 is typical of detergents

A value of 16 to 20 indicates a solubility or hydrotropic.

2.7.3 Effect of Electrolyte Concentration

Cameron (2005) found that when increase the concentration of aqueous solution of K_2SO_4 in the system composed of DVB and styrene as monomers caused a decrease of void diameter leading to emulsion stability because the propensity of Ostwald ripening is reduced. This propensity is occurred by large

droplets growing at the expense of smaller ones.. The result of Ostwald ripening is progressive coarsening of the emulsion, which leads to coalescence and, eventually, emulsion breakdown. Therefore, preventing or limiting Ostwald ripening leads to a more stable emulsion with smaller average droplet diameters.

Zhu and co-workers (2010) used poly(urethane urea) solid nanoparticle (PPU) to stabilize (pickering by adsorbing onto the interface between two phases) o/w emulsion containing acrylamide (AM) and N,N-methylene bisacrylamide (MBAM) as hydrophilic monomers and also researched the effect of NaCl concentration. It was found that when the PUU content was increased in aqueous phase, the average void diameter decreased and enhanced the stability of emulsion. Increase of NaCl concentration decreased the average void diameter.

2.7.4 Effect of Stirring Time

Zhang and co-workers (2009) researched the effect of stirring time by preparing polyHIPEs by using styrene and DVB as monomers with varying stirring time (after adding aqueous phase). Backscattering technique was used to evaluate the effect of stirring time and shown in the relation between Δbackscatering (representative of sedimentation profile) and time. It can be concluded that polyHIPE prepared with longer stirring time was very stable than the shorter one.

2.7.5 Effect of Initiator

Zhou and co-workers (2007) prepared the polyHIPE by a new method, surfactant reverse micelle method. The polyHIPE, which derived from this method, were microsphere with large macropores. The amount of initiator (Benzoyl peroxide) was investigated. It was found that, the quantity of microsphere increase with the increase of initiator because of the role of initiator is initiates polymerization reaction which leading to create the microspheres.

2.8 Applications

PolyHIPE was used as a stationary phase in a capillary tube of capillary electro chromatography (CEC) (Tunc *et al.*, 2010). In preparation, the organic phase consisted of isodecyl acrylate (IDA), divinyl benzene (DVB) as a crosslinker, and surfactant Span 80,while the aqueous phase consisted of initiator, potassium persulfate, electrolyte, $CaCl_2 .2H_2O$. The material obtained had most pore size in the range of 2-5 μm and surface area of 5.44 m^2/g with stress resistance up to 1MPa.

Poly HIPE was used for heat or fire resistant materials (Tai *et al.*, 2001). This type of material is called "hybrid foam" because it is combined with an inorganic polysilsesquioxane network, which makes good heat or fire resistance material. In this work, methacryloxypropyltrimethoxysilane (MPS) network was used, which an organic polyHIPE was made of stryrene, divinylbenzene (DVB) and span 80. The reaction was started with MPS and styrene monomers and potassium peroxodisulfate as an initiator. Then the methyl group was hydrolyzed by acid, got the hydroxyl group on structure and finally condensed to polysilsesquioxane network. In the characterization, the compressive dynamic mechanical thermal analysis (DMTA) was used to characterize thermal and mechanical properties. The modulus and T_g increase with MPS content. The mechanical behavior at low temperature (30°C) and high temperature (250°C) of poly HIPE containing MPS were failed in brittle manner. On the other hand the conventional polyHIPE was failed in ductile manner. When the MPS contents were varied, the modulus was increased with MPS. Thermo gravimetric analysis (TGA) was used to determine the decomposition temperature (T_d) of hybrid foam. Decomposition temperature values of all compositions of hybrid foam were greater than PMMA and PS material with high thermal stability materials of 220 and 300 °C, respectively.