Effect of Amines on High Internal Phase Emulsion Adsorbents for Carbon Dioxide Adsorption

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High internal phase emulsion polymers (PolyHIPE) with amine, i.e. hexylamine, were prepared. The oil-in-water emulsion system was obtained by mixing divinylbenzene, vinylbenzylchloride and surfactants, SpanR 80 (oil soluble surfactant) and Triton X-100 (water soluble surfactant). The optimum condition of the emulsion system was obtained by varying the ratio of the surfactants. The ratio of SpanR80 to Triton X-100 of 1.33 was optimum for polyHIPE, while an addition of hexylamine, the optimum was 1.50. A Fourier transform infrared spectroscope was used to confirm the presence of amine in polyHIPE by using the peak ratio change of C– vinyl at 900 to 920 cm^{-1} to C–chloride at 729 cm^{-1}. Scanning electron microscopy showed that the morphology of polyHIPE was spherical. Voids and fractures on the surface morphology were formed by agglomeration of small spheres and the surface area was a consequence of the effect of the oil soluble surfactant (SpanR80) that was dissolved into oil droplets and formed water-in-oil emulsion system.

1. Introduction

Global warming is of interest in the world society todays. Carbon dioxide is important contributor to global warming is due to a large increase of greenhouse gases, such as carbon dioxide, methane and nitrous oxide, especially the largest emission of carbon dioxide (CO_2) from industrial activities. In order to reduce CO_2 emissions into the atmosphere, a carbon capture and storage system is the most effective technology. A well-known method to capture CO_2 from flue gas is amine-based absorption, which has been widely deployed on a large scale across several industries but there are some drawbacks: (i) corrosion of plant equipment, (ii) solvent regeneration requires high energy consumption, (iii) solvent lost by evaporation, and (iv) solvent degradation. An adsorption method is one of the alternative ways. However, there are some limitations, such as low CO_2 adsorption capacity and adsorption cycles used. In order to improve the CO_2 capturing capacity onto the adsorbent surface, adsorbents with high surface area with selective adsorption to CO_2 should be used. Many types of porous adsorbents such as zeolites (Chatti et al., 2009,), mesoporous silica (Sharma et al., 2012), and fly ash (Maroto-Valer et al., 2008) were impregnated with amines, but these adsorbents show surface area reduction after amine loading due to pore plugging. The surface of adsorbents can be modified with an amine compound to increase adsorption selectivity to CO_2. This modification, amine functionalization, can be done during (pre-functionalization) or after (post-fuctionalization) adsorbent preparation (Dejburum et al., 2012). To avoid pore plugging, pre-functionalization is preferable. A promising high porous polymer called high internal phase emulsion polymers (PolyHIPE) can be prepared by water in oil or oil in water emulsion polymerization. It was possible that the amine compound could be part of the polymer structure by being introduced during emulsion polymerization. In this research, polyHIPE was prepared by oil in water emulsion polymerization using two types of surfactant (oil in water and water in oil) and amines (hexylamine) were added to the polyHIPE by pre-functionalization. Finally the polyHIPE-amine was tested for CO_2 adsorption.

2. Experimental

2.1 Materials

Divinylbenzene (DVB) used as monomer in preparation of polyHIPE, hexylamine used for functionalization with 4-vinylbenzyl chloride (VBC), potassium persulfate ($K_2S_2O_8$) used as an initiator for polymerization reaction were purchased from Merck, Germany. 4-Vinylbenzyl chloride (VBC) was purchased from Aldrich .1, 3-Diaminopropane (99 %) used for functionalization with 4-vinylbenzyl chloride and sorbitanmonooleate (SpanR80) used as surfactant in oil phase to stabilize emulsion were purchased from Sigma-Aldrich Co., USA. Triton X-100 used as surfactant in aqueous phase to stabilize emulsion system was purchased from Sigma-Aldrich Co., Switzerland. Toluene (analytical grade) and ethanol (analytical grade) were purchased from Labscan Asia Co., Ltd., Thailand.

2.2 PolyHIPE preparation

2.2.1 PolyHIPE reference preparation

The polyHIPE preparation procedure consisted of two parts, oil and aqueous phases. The first part was the oil phase. Monomers (DVB and VBC), surfactant (Triton X-100), and porogen (toluene) thoroughly mixed in a flask for 30 min. The aqueous phase were composed of the initiator ($K_2S_2O_8$), SpanR80, and water. Then, the aqueous phase was dropped into the oil phase and stirred thoroughly at room temperature for 30 minutes to obtain the emulsion. Next, the emulsion was poured into a mold and placed in an oil bath at 70 ºC for 24 h, at which time the polyHIPE solid was formed. Eventually, the polyHIPE solid was extracted by ethanol using a soxhlet apparatus for 6 hours and then dried in a vacuum at 70 ºC.

2.2.2 PolyHIPE with amines preparation

Amine was prefunctionalized with VBC in the oil phase. VBC was reacted with amine at 65 ºC for 30 minutes. A solid product was obtained. Next, it was mixed with DVB, toluene and SpanR 80. Then, the aqueous phase was added into the oil phase and stirred at room temperature for 30 minutes to form the emulsion. The emulsion polymerization procedure was repeated as described previously. The conditions for preparation of polyHIPE are presented in Table 1, where 1-5 are for varying surfactant ratio of polyHIPE reference. When the amine was added, the emulsion condition was slightly adjusted as shown in recipe 6-9 for hexylamine.

Table 1: PolyHIPE preparation conditions. The ratio of SpanR 80 to Triton X-100 was varied

Recipe	DVB (mL)	VBC (mL)	Amine (mL)	Toluene (mL)	SpanR80 (g)	Water (mL)	$K_2S_2O_8$ (g)	Triton X-100 (g)	Surfactant ratio
1	0.9	0.1	-	1	0.2	18	0.04	0.20	1
2	0.9	0.1	-	1	0.2	18	0.04	0.17	1.18
3	0.9	0.1	-	1	0.2	18	0.04	0.15	1.33
4	0.9	0.1	-	1	0.2	18	0.04	0.13	1.54
5	0.9	0.1	-	1	0.2	18	0.04	0.10	2.00
6	1.8	0.2	0.2	2	0.6	36	0.08	0.55	1.09
7	1.8	0.2	0.2	2	0.6	36	0.08	0.50	1.20
8	1.8	0.2	0.2	2	0.6	36	0.08	0.45	1.33
9	1.8	0.2	0.2	2	0.6	36	0.08	0.40	1.50

2.3 Characterization

2.3.1 Scanning electron microscopy

Scanning electron microscopy (Hitachi S-4800, Japan) was used to observe the morphology of the polyHIPE. Each sample was coated by platinum for 230 seconds. The magnifications of the images were 10K, 20K, 50K, and 100 K.

2.3.2 Fourier transformation infrared spectroscopy (FTIR)

Fourier transformation infrared spectroscopy (Thermo Nicolet Nexus 670, USA) was used to characterize the reaction of VBC and amine.

2.3.3 Surface area analysis

The Brunauer, Emmett, and Teller (BET) technique was used to perform on the Autosorb-1MP (Quantachrome, USA). The polyHIPE was dried in a vacuum oven overnight at 70 °C before out gassing at 110 °C. The specific surface area of polyHIPE was performed using nitrogen adsorption.

2.3.4 Carbon dioxide adsorption

An experimental setup (Figure 1) with premixed 15 % CO_2/N_2 and pure N_2 coming from the two gas cylinders controlled by mass flow controllers were mixed in the mixing chamber to obtain 4 % CO_2. The mixed gas was then controlled to a fixed pressure for ventilation and enabling small quantity of 4% CO_2 gas to pass through the rotameter which the flow rate was adjusted to 3 mL/min and determined by the bubble flow meter. The adsorption column was a tubular glass flow adsorber with the dimension of 4mm id x 6mm od x 39 cm length vertically oriented for the evenly distribution of the adsorbent. The column was wounded with an insulator of 40 cm long to maintain constant room temperature (25 °C) throughout the whole experiment. From the top 18.5 cm of the column, the adsorbent (0.25 g) was packed and emplaced with the glass wool at the top and the bottom to support the adsorbent, so the feed was running against gravity.
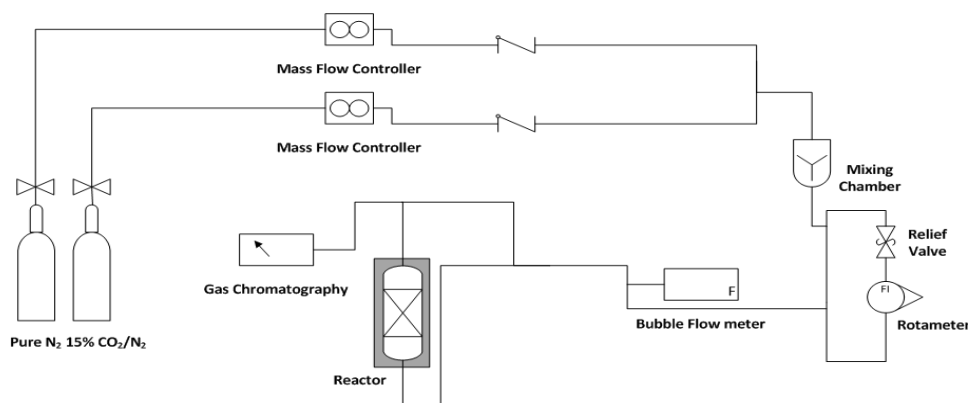

Figure 1: Schematic flow diagram for CO_2 adsorption (Kangwanwatana, 2013)

For gas chromatography-thermal conductivity detector (GC-TCD) operation, Rt®-Q-BOND column with 0.53 mm id x 20 µm film thickness x 30 m length was used to operate at an isothermal temperature of 40 °C. The GC injection port was heated to 100 °C with the spilt flow of 8 mL/min and helium as a carrier gas. In typical CO_2 adsorption, 0.25 g of adsorbent in the column was pre-dried at 60 °C for 1 h while purging with N_2 gas at 113 mL/min. Then, 4 % premixed CO_2 of dry gas at 3 mL/min was allowed to flow into the packed bed adsorber to carry out the experiment at room temperature and atmospheric pressure until the CO_2 concentrations of the feed gas at the outlet of adsorber reached equilibrium. The concentrations of CO_2 in the downstream in terms of chromatogram were continuously monitored with a computer program, WiniLab III V4.6. The dynamic adsorption capacity of the adsorbent (Q_{ads}) was calculated with Eq(1),

$$Q_{ads} = \frac{FC_{in}t_{st}}{M} \qquad (1)$$

where F (mol/min) is the total molar flow of feed gas, C_{in} is the CO_2 concentration of the inlet stream, M is the mass of solid adsorbent loaded in the column, and t_{st} (min) is the stoichiometric time which was determined from the breakthrough curve according to Eq(2) via MATLAB software.

$$t_{st} = \int_0^t (1 - \frac{C_{ou}}{C_{in}})dt \qquad (2)$$

where C_{in} and C_{ou} are the CO_2 concentrations of inflow and outflow gas stream of the column.

3. Results and discussion

3.1 PolyHIPE reference

PolyHIPE reference was prepared first and used as a reference for guideline to synthesize the polyHIPE with hexylamine. The surfactant ratio (SpanR80: Triton X-100) was varied from 1.00 – 2.00. Figure 2 shows spherical shape with void and fracture appearance. The surface roughness was formed by agglomeration of small spheres. The surface area was evidently affected by void and fractures on the surface. The particle size was in a range of 1-2 µm.
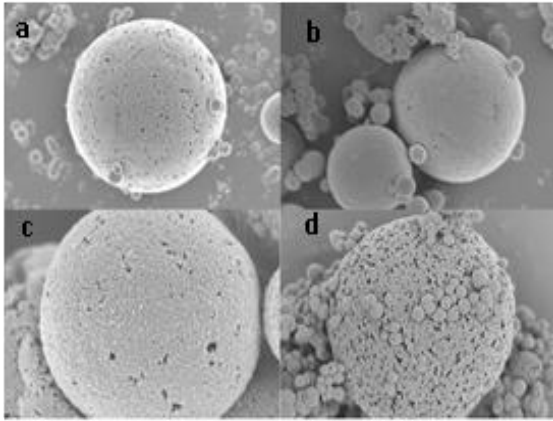
Figure 2: SEM micrographs of PolyHIPE Reference with magnification x20K, surfactant ratio of a) 1.0, b) 1.18, c) 1.33, d)1.54
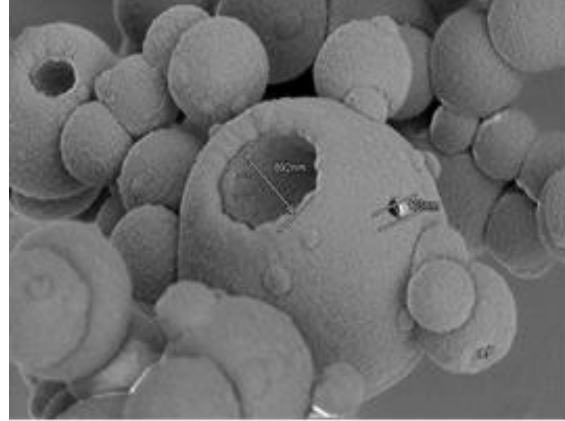

Figure 3: SEM micrographs of PolyHIPE reference, surfactant ratio of 2 at x50K

When the surfactant ratio was increased to 2, the void and fracture on the surface was larger than that of the lower surfactant ratio as shown in Figure 3. An agglomeration of polyHIPE or inconstant shape was observed at a very high surfactant ratio, as shown in Figure 4. The void and fracture of the sphere was created as demonstrated, in Figure 5, for water in oil in water (w/o/w) emulsion where water droplet was stabilized by the oil soluble surfactant inside the oil droplet of the emulsion (w/o) of the oil droplet in water (w/o/w) emulsion. At a low concentration of oil soluble surfactant, but still higher than the critical micelle concentration (cmc) of SpanR80, the simple spherical reverse micelle was formed. The reverse micelle sphere trapped water inside, after the emulsion polymerization and the water was removed, the void was consequently formed. At high oil soluble surfactant concentration, spherical micelles could probably be transformed to different reverse micellar shapes, such as lamellar and bilayer etc., which resulted in different structure of polyHIPE as shown in Figure 3 (Zhou et al., 2007). In addition, the change of surfactant ratio also affected the surface area of polyHIPE. As shown in Table 2, the surface area was maximum where the surfactant ratio was in the range of 1.18 – 1.33 and decreased beyond this range.
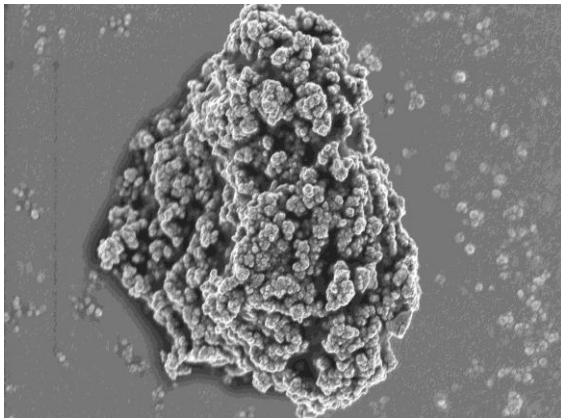

Figure 4: SEM micrograph of polyHIPE reference at surfactant ratio of 4 and x 20K
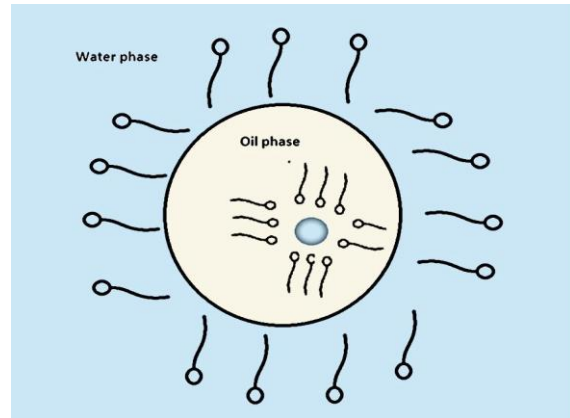

Figure 5: Void and fracture formation from the effect of oil soluble surfactant

Table 2: Surface area of polyHIPEs

Recipe	Surfactant ratio	Surface area (m^2/g)
1	1.00	91.28
2	1.18	106.00
3	1.33	102.60
4	1.54	89.38
5	2.00	65.16

3.2 PolyHIPE with amines

Hexylamine was reacted with VBC to make sure there was a complete reaction before mixing in the oil phase and in the emulsion polymerization process. To confirm the reaction between VBC and the amine, the product was characterized by FTIR as shown in Figure 6.
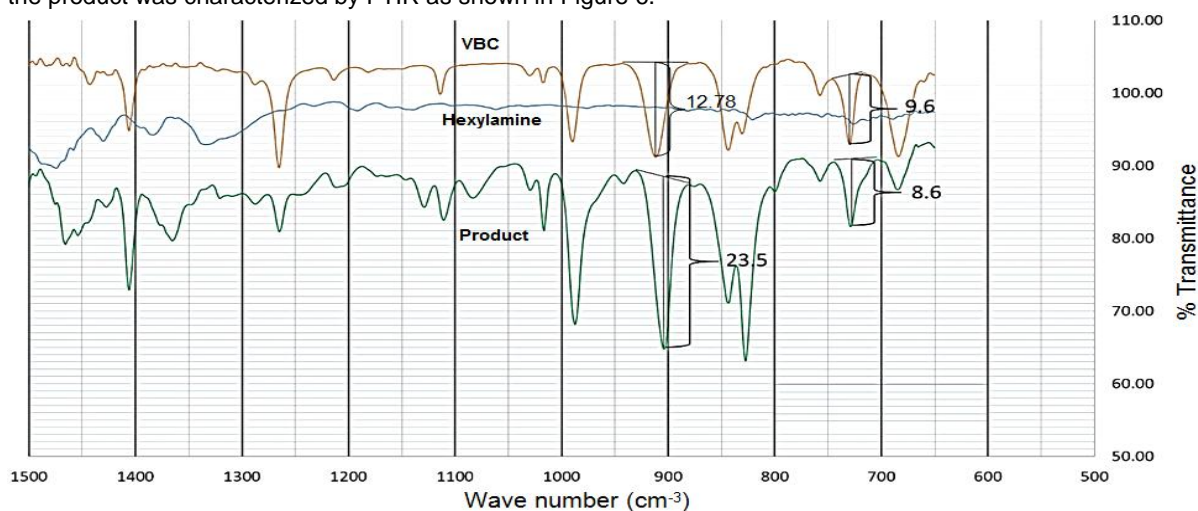

Figure 6: FTIR spectra of hexylamine, VBC, and VBC-hexylamine product.

Spectrum of VBC shows characteristic bending vibrations of the vinyl group at 911 cm^{-1} and C-Cl stretching at 729 cm^{-1}. The peak intensity ratio of these two peaks is constant. In the presence of hexylamine, the reaction takes place between the amine group of hexylamine and chloride group of VBC. As the result, the peak intensity of C-Cl stretching decreases correspondingly with the reaction and thus, the decrease of the peak intensity ratio of 729 cm^{-1} to 911 cm^{-1} can be used to confirm the reaction. The conversion of polyHIPE to polyHIPE-amine was 51.27 %. Figures 7 and 8 show SEM micrographs of polyHIPE with hexylamine. There is the formation of spherical shapes similar to that of the polyHIPE reference, which indicates the same mechanism of void and fracture formation on the surface.

The surface area of polyHIPE-hexylamine is shown in Table 3. The highest surface area (88.05m^2/g) was obtained from the surfactant ratio of 1.50 (recipe 9). The optimum ratio was slightly increased from the polyHIPE reference (1.18-1.33) because a larger amount of monomers, derived from VBC and hexylamine, required more surfactant quantity. It was noted that the addition of amine into the highly porous structure of polyHIPE did not change the surface area of the adsorbent. The surface area of the polyHIPE-hexylamine reference (88.05 m^2/g) was very similar to that of polyHIPE reference (89.38 m^2/g) at a similar surfactant ratio of 1.5.
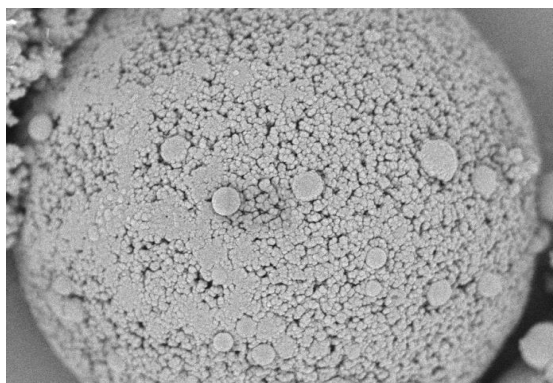

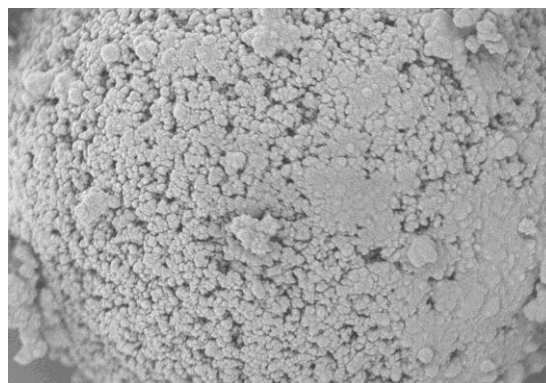*Figure 7: SEM of polyHIPE with hexylamine at surfactant ratio of 1.50 and magnification x20K*

Figure 8: SEM of polyHIPE with hexylamine at surfactant ratio 1.33 and magnification x20K

3.3 CO_2 adsorption

The CO_2 adsorption capacity was measured and shown in Table 3. The highest CO_2 adsorption capacity of 0.0681 mmol/g was obtained from the surfactant ratio of 1.50.

Table 3: Surface area of polyHIPE-hexylamine and CO_2 adsorption capacity

Recipe	Surfactant ratio	Surface area (m^2/g)	CO_2 adsorption capacity (mmol/g)
7	1.20	17.77	0.0436
8	1.33	38.75	0.0584
9	1.50	88.05	0.0681
10	1.71	25.63	0.0561

4. Conclusions

The spherical polyHIPE with the void and fracture surface was synthesized from water in oil in water (w/o/w) emulsion by varying the quantity of oil soluble surfactant to water soluble surfactant in the ratio range of 1-2. The addition of hexylamine slightly shifted the spherical formation with void and fracture condition of polyHIPE reference to obtain the highest surface area of polyHIPE-hexylamine. The amine loading by high internal phase emulsion polymerization showed that there was no decrease in surface area or pore plugging, which was considered to be an advantage of the method. The preliminary results of the CO_2 adsorption capacity was low (0.0681 mmol/g), which still could be improved by increasing amount of hexylamine in the emulsion polymerization step.

5. Recommendations for further study

The following suggestions are given for future studies:
- Synthesize polyHIPE with a different type of polyamine, such as 1,3-diaminopropane. Then, compare the properties including the CO_2 adsorption ability with the polyHIPE reference and polyHIPE with hexylamine.
- Investigate the effect of moisture on adsorption capacity of all polyHIPE types.
- Increase quantity of amine loading in polyHIPE.

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