

Polyethyleneimine Loading into High Internal Phase Emulsion Polymer for CO₂ Adsorption: Synthesis and Characterization of the PolyHIPE

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The purpose of this research was to synthesize the new type of adsorbent for CO₂ adsorption. The polymer obtained from high internal phase emulsion or “polyHIPE” can be polymerized from divinylbenzene (DVB) and vinyl benzyl chloride (VBC). Polyethyleneimine (PEI) was added into the polyHIPE during polymerization reaction to increase the CO₂ capture efficiency. For the effect of the monomer ratio (DVB/VBC), the polyHIPE for every ratio has the same appearances which are white, brittle and chalky porous solid. The surface area of the polyHIPE increased when the amount of DVB was increased. The highest surface area was found in the monomer ratio of 100/0 or 100 % DVB, which was 303.0 m²/g. When 10 wt% PEI was added into the polyHIPE, the percentage of PEI loading was very low at 100/0 monomer ratio; there was only 0.11 wt% of PEI. As the ratio of VBC increased from 10 % to 50 %, the percentage of PEI loading in the polyHIPE was increase up to 1.7 wt% and then stayed almost constant because 10 wt% PEI can react completely with 1.26% VBC. Moreover, when the percentage of PEI in the prepared solution was increase, the percentage of PEI in polyHIPE was also increase, and the highest percentage of PEI in polyHIPE was 2.57 wt%.

1. Introduction

Since the industrial revolution in 1850s began, industrial processes, mainly from the combustion of fossil fuels, have caused emissions of greenhouse gas. The most important greenhouse gas is carbon dioxide (CO₂) that caused global warming. One of the interesting technologies that can be used to reduce CO₂ emission is CO₂ capture via post – combustion (Thiruvengkatachari et al., 2009). Nowadays, one of the best CO₂ capture technologies is the absorption process using amine solution, but amine solutions still have some problems associated such as solvent degradation and corrosion. Therefore, alternative methods have been developed, for example adsorption process using adsorbents like, activated carbon, zeolites and polymers (Yang, 2003).

In adsorption process, molecules of CO₂ are adsorbed onto a surface of adsorbent. Adsorption is caused by Van der Waals Force which exists between molecules. This force is extremely effective only in short ranged and therefore sensitive to the distance between the adsorbent surface and the adsorbate molecule. In general, the adsorbability of a compound increases with: increasing molecular weight or contact area between adsorbent and adsorbate, a higher number of functional groups, and increasing polarizability of the molecule (Brandt et al., 1993).

In this research, the polymer obtained from high internal phase emulsion or “polyHIPE” is focused because it contains many advantages, i.e., very high surface area which is one of the important

properties of the adsorbent. Another advantage is that polyHIPE is very flexible to processed into any form needed (Cameron, 2005). In addition, adsorption efficiency can also be increased by the amine functional groups on the adsorbent. Thus, polyethyleneimine (PEI) is in focused because PEI is one of the polymers containing amine functional group in the structure that can be used to capture CO₂. Most PEI adsorbents have been prepared by impregnation onto porous material, which PEI can plug the pore (Xu et al. 2002). Furthermore, interaction between PEI and the adsorbent surface is low, therefore PEI can be lost during the regeneration process.

The goal of this research is to add PEI into polyHIPE directly during the polymerization reaction to gain advantages, such as maintaining high surface area and effective amine functional group of PEI.

2. Methodology

2.1 Equipments

Fourier transform infrared spectrophotometer (FT-IR), Nicolet/Nexus 670 Model (Massachusetts, USA) was used to characterize the functional group of the adsorbent. Scanning electron microscope (SEM), Hitachi/S - 4800 Model (Ontario, Canada), was used to characterize the surface morphology of the adsorbent. Surface area analyzer (AS 1-MP), Quantachrome/ Autosorb 1-MP Model (Florida, USA) was used to characterize surface area. Ultraviolet–visible spectrophotometer (UV-VIS), Shimadzu, UV-VIS Spectrometer 2550 Model (Tokyo, Japan) was used to measure the amount of PEI loaded into polyHIPEs.

2.2 Chemicals

An oil phase consisted of divinylbenzene (80% DVB), supplied by Merck Schuchardt, and vinyl benzyl chloride (90 % VBC), supplied by Aldrich, as monomers. Mixed surfactants included sorbitan monooleate (Span 80, supplied by Fluka), cetyl trimethylammonium bromide (CTAB, 96%, supplied by Fluka) and dodecylbenzenesulfonic acid sodium salt (DDBSS, supplied by Aldrich). Toluene (99.5 %, supplied by RCI Lab scan) was used as a porogen. An aqueous phase consisted of potassium persulphate (K₂S₂O₈, 99 %, supplied by Merck Schuchardt) as an initiator. Calcium chloride dihydrate (CaCl₂.2H₂O, supplied by J.T. Baker Chemicals) was an electrolyte. Polyethyleneimine (PEI, 50 wt% in water, Mn 1200, Mw 1300) was supplied by Aldrich. Distilled water was used as an internal phase. Ethanol (99.9%, supplied by RCI Lab scan) was used for washing polyHIPEs via soxhlet extraction and salicyladehyde (98%, supplied by Fluka) was used to determine the amount of PEI loading.

2.3 Preparation of PolyHIPE

Preparation of polyHIPE was divided into two phases, oil phase and aqueous phase. In the oil phase, mixture of surfactants (0.36 g. of SPAN80, 0.0224 g. of CTAB and 0.0171 g. of DDBSS), porogen (1 mL toluene) and monomers (DVB+VBC, a total volume of 1 mL) were added into flask and then the solution was stirred (700 rpm) at room temperature for 30 min. The aqueous phase contained initiator (0.04 g. K₂S₂O₈), electrolyte (0.2 g. CaCl₂.2H₂O), and water (18 mL).

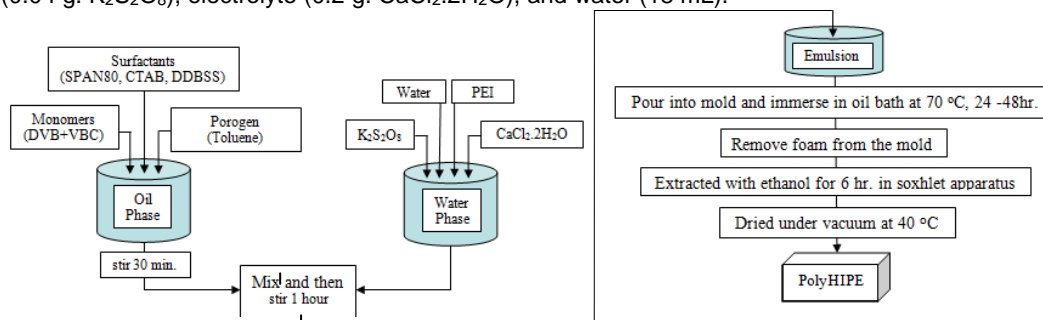


Figure 1: Methodology flow diagram

Then, the aqueous phase was slowly added into the oil phase while being stirred (700 rpm) at room temperature for an hour until the system became emulsion. Finally, the emulsion was poured into a mold and immersed in a water bath at 70 °C for 24 h to allow polymerization to complete to form

polyHIPE. Finally, the solid polyHIPE was removed from the mold, left outside until dry, and washed with ethanol for 6 h in a soxhlet apparatus. Solid foams were then dried under vacuum at 40 °C overnight and then kept in a desiccator. The methodology flow diagram is shown in Figure 1.

2.3.1 Effect of Monomer Ratio on PolyHIPEs

To obtain the most suitable monomer ratio, various volume ratios of DVB/VBC were used, i.e., 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50, with a total volume of 1 mL and the polyHIPEs was prepared as described previously.

2.3.2 Effect of PEI Loading on PolyHIPEs

When the most suitable monomer ratio was obtained, the amount of PEI loaded on polyHIPEs was studied by varying the amount of PEI added into the polyHIPEs, i.e., 0, 5, 10, 15, 25 and 30 wt% related to weight of monomer. The first step was the preparation of stock solution of 30 wt% PEI by dissolving 7.6170 g of 50 wt% PEI solution in distilled water, and adjusting the volume of solution to 250 mL. For lower wt% PEI, the 30 wt% PEI stock solution was diluted to desired concentrations by using Eq. 1 to calculate the volume of 30 wt% PEI solution needed. The second step was a preparation of the aqueous phase by weighing $K_2S_2O_8$ and $CaCl_2 \cdot 2H_2O$ followed the preparation of polyHIPE.

$$C_1V_1 = C_2V_2 \quad (1)$$

2.4 Characterizations

2.4.1 Surface Morphology Study of PolyHIPEs

Scanning electron microscope (SEM), was used to analyze the morphology and porous features of polyHIPEs. The condition of the analyzer was: voltage of 5 kV, current of 10 mA, and magnification of 1k, 3k and 10k. Samples were coated with platinum under vacuum before observation to make them electrically conductive.

2.4.2 Surface Area Measurement of PolyHIPEs

Specific surface area and pore size distribution were characterized by BET nitrogen adsorption/desorption measurements with a surface area analyzer. The samples were out gas at temperature 120 °C for 8 – 10 hours until the outgas pressure rise limit was lower than 10 micron/min. For the characterization method, a full isotherm of macropore was used.

2.4.3 Functional Groups Analysis of PolyHIPEs

Fourier transform infrared spectrophotometer or FTIR was used to determine N-H stretching at 3400-3380 cm^{-1} and 3345-3325 cm^{-1} , N-H bending vibration at 1650-1550 cm^{-1} and C-Cl vibration at 1260 cm^{-1} . Firstly, 0.0030 g of polyHIPE was ground and mixed with 0.0100 g potassium bromide (KBr), and then the mixture was transferred into a mold and compressed into pellet. The obtained pellet was placed in an IR sample holder and in the sample compartment. The measurement was carried out in a transmission mode with 16 resolutions, 64 numbers of scans in a range of wave number from 400 to 4000 cm^{-1} by using air as a background. For PEI solution sample, the PEI solution was dried and then 0.0030 g of dried PEI sample was ground and mixed with 0.0100 g KBr. The measurement was carried out in the same mode as polyHIPE samples.

2.4.4 PEI Loading Analysis

The amount of PEI present in polyHIPE was determined by ultra violet-visible spectrophotometer or UV-VIS. The polyHIPE samples were ground, accurately weighed of 0.0300 g and then immersed in 100 mL of 0.02M solution of salicylaldehyde in a solvent mixture of methanol/1% acetic acid aqueous solution (80/20, v/v). After 24 h, the mixture was filtered. 1 mL of the filtrate was diluted for 400 times with the solvent mixture of methanol/1% acetic acid aqueous solution (80/20, v/v). The UV absorbance at 255 nm was measured and converted to the residual concentration of salicylaldehyde by using calibration curve as shown in Figure 2.

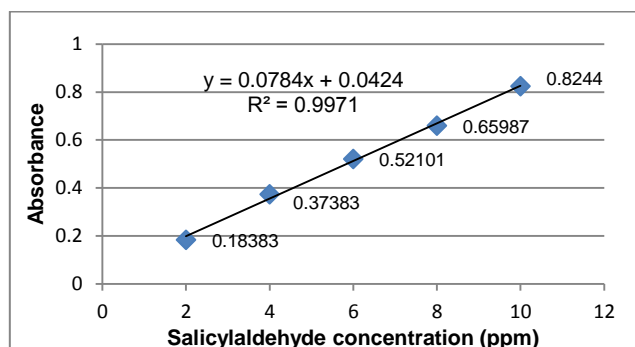


Figure 2: UV-VIS calibration curve

3. Results and Discussion

3.1 Effect of Monomer Ratio to the Properties of PolyHIPE with and without PEI Loading

The SEMs of polyHIPEs with different DVB/VBC ratios are shown in Figure 3. When the amount of DVB in the monomer ratio increases, the void diameter decreases due to DVB being a cross-linking agent. When the amount of DVB increases, it makes the polymer structure denser and leads to the decreasing of void diameter. Moreover, the amount of DVB corresponds to the surface area of the polyHIPE. When the amount of DVB increases, the surface area is increased, as shown in Table 1.

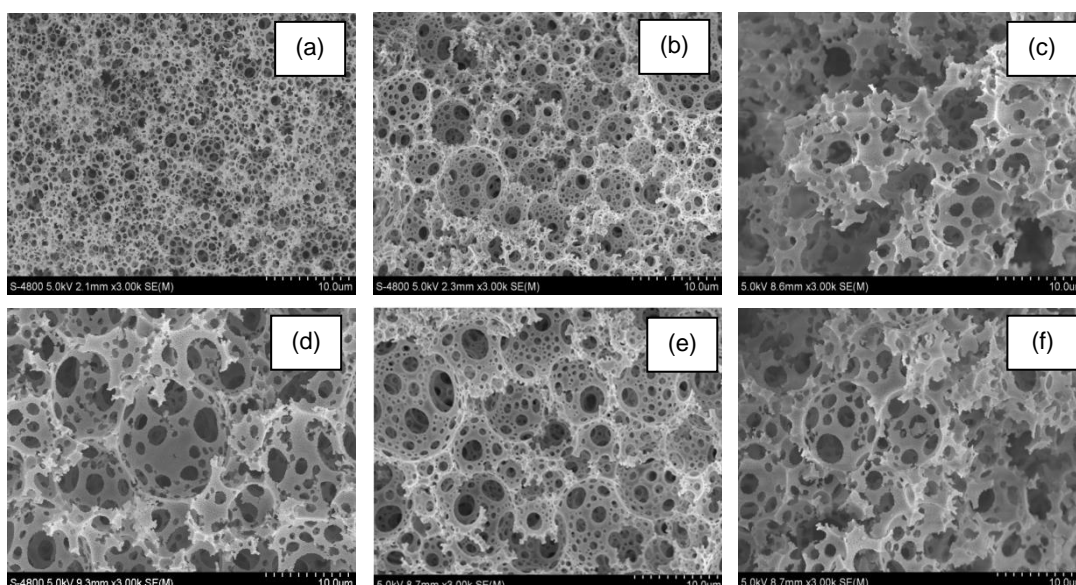


Figure 3: SEMs of polyHIPE without PEI loading and different DVB/CBV ratio of (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40 and (f) 50/50

Table 1: Surface area of polyHIPEs

PolyHIPEs (DVB/VBC)	Surface area (m ² /g)
50/50	57.3
60/40	93.2
70/30	142.5
80/20	180.0
90/10	210.0
100/0	303.0

When 10 wt% of PEI was loaded into the emulsion with different monomer ratios, the results are shown in Table 2, with approximately the same amount of PEI was loaded. The SEMs illustrated in Figure 4 shows that PEI can hardly be seen in the monomer ratio of 100/0 whereas in other ratios, PEI can be seen clearly. This was due to chloride group in VBC being replaced by amine in PEI and formed a chemical bond. However, there was very small amount of PEI being loaded into the polyHIPE with monomer ratio 100/0 because PEI cannot form a chemical bond with DVB so, when the polyHIPE was washed with ethanol, PEI was also washed out. However, there was very small amount of PEI remaining in the polyHIPE probably due to the inadequate soxhlet extraction time to wash out all PEI. From the calculation, 10 wt% of PEI reacts completely with 1.26 %v/v of VBC, therefore, the amount of PEI loading depends on the amount of VBC. However, when the amount of VBC increases, the viscosity of the emulsion increases. Moreover, when PEI is added into the emulsion, the emulsion viscosity is increased. Thus, the monomer ratio of 60/40 was selected for the study of different amount of PEI loading due to the optimum viscosity.

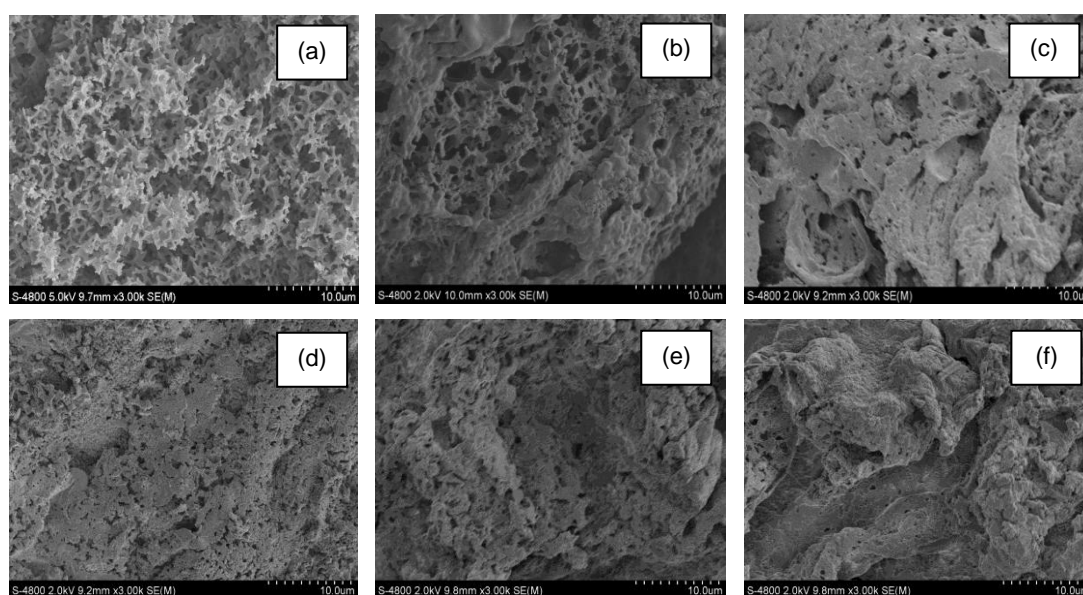


Figure 4: SEMs of polyHIPE with 10 wt% PEI loading and different DVB/CBV ratio of (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40 and (f) 50/50

Table 2: UV-VIS results

Solution	Absorbance at 255 nm	Percent of amine in polyHIPE (%)
100/0, 10% PEI	0.570	0.11
90/10, 10% PEI	0.468	1.71
80/20, 10% PEI	0.470	1.68
70/30, 10% PEI	0.475	1.60
60/40, 10% PEI	0.468	1.71
50/50, 10% PEI	0.474	1.61

3.2 Effect of PEI Loading

The percentage of PEI loading into polyHIPE (DVB/VBC ratio 60/40) was varied from 0-30 wt%. However, when the percent of PEI is greater than 20 wt%, the emulsion cannot be stirred due to the viscosity of the emulsion being too high. The amount of PEI loading, as shown in Table 3, indicated that when the concentration of PEI solution increases, the amount of PEI loading increases, up to 2.57 wt%. The SEMs as shown in Figure 5 also indicates that when the concentration of PEI solution

increases, more porous structure of the polyHIPE are covered by PEI leading the decreasing of the surface area. The BET results are shown in Table 4.

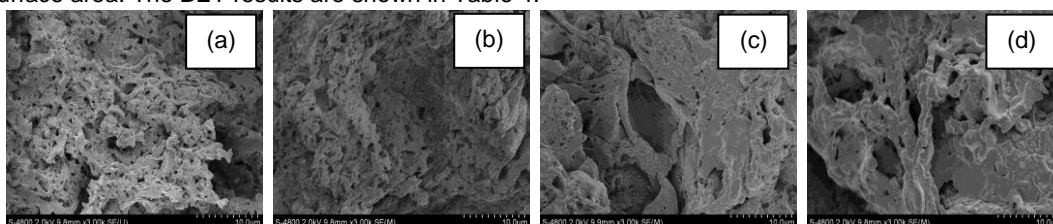


Figure 5: SEMs of polyHIPE with monomer ratio 60/40 and different percent of PEI, (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt%

Table 3: UV-VIS results

Solution	Absorbance at 255 nm	Percent of amine in polyHIPE (%)
60/40, 5% PEI	0.488	1.39
60/40, 10% PEI	0.462	1.80
60/40, 15% PEI	0.446	2.05
60/40, 20% PEI	0.413	2.57

Table 4: BET results

PolyHIPEs (DVB/VBC)	Surface area (m ² /g)
60/40, with 5% PEI	30.4
60/40, with 10% PEI	21.2
60/40, with 15% PEI	11.1
60/40, with 20% PEI	6.3

4. Conclusion

The surface area of the polyHIPE increases when the amount of DVB increases. The monomer ratio providing highest surface area is 100% DVB, which is 303.0 m²/g. When PEI was loaded into the polyHIPE, the surface area decreased. The highest percentage of PEI loading is 2.57wt% at the monomer ratio of 60/40, corresponding to the surface area of 6.3 m²/g.

Acknowledgement

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