SURFACE MODIFICATION OF POLYHIPEs USING SOLUTION PLASMA PROCESS FOR CO₂ ADSORPTION

Mookyada Mankrut a, Jitima Preechawong a, Manit Nithitanakul a

a The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

Keywords: PolyHIPEs, carbon dioxide adsorption, polyethyleneimine, solution plasma process

High internal phase emulsion polymers (polyHIPEs) are highly porous polymers prepared by high internal phase emulsion (HIPE) technique. Because of their characteristics, i.e. high surface area and high porosity with interconnecting pores, polyHIPEs have been widely used in such applications as adsorbents, membranes, scaffolds in tissue engineering and sensing materials. In this work, polyHIPE derived from divinylbenzene was prepared and the polyHIPE was modified with polyethyleneimine (PEI) by using solution plasma process. These modified polyHIPE will be then used as an adsorbent for CO₂ adsorption study. The existence of amine groups on the surface of samples was confirmed by Fourier transform infrared (FTIR) spectroscopy and water contact angle measurement, which showed that contact angle of polyHIPEs decreases after surface modification. The use of scanning electron spectroscopy (SEM) to investigate the morphology of samples revealed that unmodified and PEI-modified polyHIPEs showed an open porous structure with interconnecting pores.

email: Manit.n@chula.ac.th

INTRODUCTION

An increase in anthropogenic carbon dioxide (CO₂) emission has been a current concerned environmental problem because CO₂ is the major cause of the global warming. The main sources of CO₂ emission are burning of fossil fuels and industrial processes. CO₂ capture and storage approach is one of the most feasible ways to mitigate the concentration of CO₂ released to the atmosphere (Olivares-Marín and Maroto-Valer 2012). Such an approach consists of various techniques including solution absorption, adsorption process, membrane separation and, cryogenic distillation (Wang and Li 2014). Absorption technique using aqueous solution containing water-soluble amine, e.g. monoethanolamine (MEA), is mostly used for CO₂ capture. This is due to its high carbon dioxide absorption efficiency. Nevertheless, such a technique possesses some detrimental aspects: high energy consumption in regeneration process, sorbent degradation and, equipment corrosion (Goeppert, Czaun et al. 2011). To overcome these problems, adsorption process is offered. In this process, CO₂ molecules are captured using a porous material with high surface area. For instance, activated carbon, zeolite, mesoporous silica (Li, Duan et al. 2013) as well as porous polymers called high internal phase emulsion polymers (polyHIPEs).

PolyHIPEs are porous polymers produced by polymerization of high internal phase emulsion (HIPE), which is normally composed of two phases: internal (disperse) phase and external (continuous) phase. These porous polymers provide high surface area and high porosity with interconnecting pores. Therefore, polyHIPEs are used in such applications as adsorbents, separation membranes, supporting materials and scaffolds for tissue engineering (Silverstein and Cameron 2002).
In CO₂ adsorption application, amine-based adsorbents have been mostly investigated. This is because of the high CO₂ uptake, which results from chemisorption between active sites, amine functional groups, and CO₂ molecules (Li, Duan et al. 2013). There are relevant of amines have been utilized for solid amine adsorbents such as alkanolamine, alkylamine, aminosilane and, polymer containing amine functional groups. Polyethyleneimine (PEI) is widely used for amine-modified adsorbents because it contains a large number of amine groups which can lead to high adsorption capacity (Wang, Yao et al. 2016). Moreover, the CO₂ adsorption capacity also depends on types of amine functional groups. It was found that the adsorption capacities of amine-based adsorbents were in the order of primary > secondary > tertiary amine containing in the adsorbent (Saiwan, Muchan et al. 2013).

Surface modification is a practical way to introduce functional groups to the surface of porous substrates. So far, various surface modification techniques have been proposed such as physical impregnation, chemical grafting, layer-by-layer and, plasma treatment process. Solution plasma process (SPP), one type of plasma treatment processes, has been reported for using in surface modification. This process involves an electrical discharge plasma in a liquid phase and possesses a fast reaction speed. Unlike air-plasma process, SPP allows the active species to enter the geometrically hindered sites, narrow pores, of porous materials (Joshi, Schulze et al. 2009). SPP is also widely used in nanomaterial synthesis, water treatment, sterilization and degradation of organic compounds (Takai 2008).

The objective of this work was to modify polyHIPEs with polyethyleneimine solution by using solution plasma process to produce the adsorbents for CO₂ adsorption study, and also to investigate the CO₂ adsorption performance of PEI-modified polyHIPEs.

EXPERIMENTAL

A. Materials
Divinylbenzene (DVB, Aldrich; 80%), sorbitan monooleate (Span 80; S80, Aldrich), toluene (Labscan), potassium persulfate (KPS; K₂S₂O₈, Fluka), calcium chloride dehydrated (CaCl₂·2H₂O, Fluka), polyethyleneimine (PEI, Aldrich; 50 wt% in water, Mn 1800, Mw 2000) were purchased from various suppliers and used as received. Deionized (DI) water was used as an internal phase. Isopropanol (ISO, Labscan) and distilled water were used for washing polyHIPEs in soxhlet extraction.

B. PolyHIPE Preparation
DVB as a monomer, toluene as a porogenic solvent and, Span 80 as a surfactant were mixed to form an oil phase. DI water, CaCl₂·2H₂O as a stabilizing salt, and KPS as an initiator were mixed to form an aqueous phase. The mixture of aqueous phase was slowly dropwise to the mixture of oil phase to form HIPE under constant stirring. The formed HIPE, white slurry, was poured into cylindrical glass molds and then placed in a water bath for polymerization at 70°C for 48 hours. The resulting polyHIPEs were removed from molds and then dried in an oven at 60°C for 24 hours. The unreacted monomer, remaining solvent and surfactant were removed by soxhlet extraction, first with isopropanol for 6 hours followed by distilled water for 6 hours, and then polyHIPEs were dried in an oven at 60°C until a constant weight was obtained.
C. PEI-modified PolyHIPE Preparation

The resulting polyHIPEs were cut into small pieces (8 mm thick) and then placed in a glass chamber containing 80 cm$^3$ of PEI solution. The sample was hung approximately 1 cm over the plasma zone. Two electrodes made of tungsten were used. An alternating current with frequency of 30 kHz, a pulsed width of 1.6 μs, and a high voltage were applied. The plasma exposure time was varied at 5, 10 and 15 min.

![Solution plasma reactor setup.](image)

**Figure 1** Solution plasma reactor setup.

D. PolyHIPE Characterizations

*Morphological structure.* The morphology of samples was investigated using a field emission scanning electron spectroscopy (FE-SEM, Hitachi S-4800). Samples were sputter-coated with platinum in a sputter coater prior to an analysis.

*N$_2$ adsorption-desorption.* The surface area and pore size were measured by N$_2$ adsorption-desorption isotherm using Quantachrome Autosorp-1. The surface area was calculated using Brunauer-Emmett-Teller (BET) method. Prior to each measurement, sample was degassed at 110ºC for 24 h.

*Fourier transform spectroscopy (FT-IR).* The characteristic functional groups of samples were determined by FT-IR spectra recorded using a Nicolet Nexus 670 FT-IR spectrometer. The solid sample was ground with potassium bromide (KBr) and compressed into a pellet. The spectra were collected over a wavenumber range of 4000-650 cm$^{-1}$ with accumulating 64 scans at an effective resolution of 2 cm$^{-1}$.

*Wetting ability.* The static water contact angle of samples was measured in sessile drop mode using a contact angle instrument (Krüss, model DSA 10) to investigate the change in wetting ability of polyHIPEs after surface modification.

**RESULTS AND DISCUSSION**

A. Morphological Structure

The surface morphology of unmodified polyHIPEs was illustrated in Figure 2a. SEM micrograph shows open cell structure with interconnecting pores. The resulting polyHIPEs
had BET surface area of 330.7 m²/g, pore size of 0.007307 μm and, pore volume of 0.6042 cm³/g.

Figure 2  SEM micrographs of (a) unmodified polyHIPE and PEI-modified polyHIPEs for different plasma exposure time; (b) 5 min, (c) 10 min and (d) 15 min; with magnification of x500.

After surface modification using solution plasma process, the SEM micrographs shows no alteration in morphological structure in spite of increasing in plasma exposure time, as shown in Figure 2b-2d.

B. Surface Chemical Composition

The main absorption bands for unmodified polyHIPEs (Figure 3a) were found at 2927 and 3021 cm⁻¹ (Gomes and Bhaumik 2015). The strong band at 2927 cm⁻¹ was assigned to methylene C-H stretching whereas the band at 3021 cm⁻¹ originated from aromatic stretching vibration. In Figure 3, the broad band at wavenumber region of 3700-3200 cm⁻¹ may be due to the overlapping of O-H and N-H stretching, however, the characteristic band of N-H stretching vibration is found at wavenumber ranging from 3500 to 3300 cm⁻¹ (Sun, Wang et al. 2011). Besides, the band at 1660 cm⁻¹ corresponds to N-H bending vibration (Dejdurum P. 2012). In Figure 3b, the presences of N-H stretching vibration at region from 3700 to 3200 cm⁻¹ and N-H bending at 1660 cm⁻¹, similar to the top surface of PEI-modified polyHIPEs, indicating that amine groups were introduced to the inner pores of polyHIPEs.
C. Changes in Surface Wettability

The water contact angle of unmodified and PEI-modified polyHIPEs is shown in Figure 4. The results showed that surface modification using solution plasma process caused a decreasing in water contact angle with increasing in plasma exposure time.

The reduction of water contact angle indicated a more hydrophilic, resulting from the formation of hydrophilic groups on the polyHIPEs surface.

CONCLUSION

PolyHIPEs derived from divinylbenzene were successfully prepared using high internal phase emulsion technique. The resulting polyHIPEs were modified with polyethyleneimine solution using solution plasma process in order to introduce amine functional groups to the surface of polyHIPEs for CO\textsubscript{2} adsorption study. The FTIR spectra and decreasing in water contact angle indicated the presence of amine groups on polyHIPEs surface. As a result, PEI-modified polyHIPEs would exhibit higher CO\textsubscript{2} adsorption capacities, comparing to those of unmodified polyHIPEs. The further process is to investigate the CO\textsubscript{2} adsorption performance of PEI-modified polyHIPEs.
ACKNOWLEDGEMENTS

Authors would like to express gratitude to the Petroleum and Petrochemical College of Chulalongkorn University and NU-PPC Plasma Chemical Technology Laboratory.

REFERENCES


Saiwan, C., Muchan, P., deMontigny, D., Tontiwachwutikul, P., Functionalization of poly(high internal phase emulsion) with amine for co2 capture. Chemical Engineering Transactions, 35, 391-396.


