

CHAPTER IV

Highly Porous Polymeric Foam of Maleimide-Terminated Poly(arylene ether sulfone) Oligomers via High Internal Phase Emulsions

4.1 Abstract

PolyHIPEs are highly porous polymers which can be synthesized through emulsion templating by polymerizing the continuous phase of high internal phase emulsions (HIPEs). Poly(arylene ether sulfone) oligomers were synthesized via nucleophilic aromatic substitution reaction of bisphenol A, 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI), and bis-(4-chlorophenyl)-sulfone were introduced to copolymerize with DVB to improve CO₂ adsorption and the mechanical properties of obtained materials. A maleimide-terminated aryl ether sulfone oligomer (MAPES) was copolymerized with divinylbenzene (DVB) in the continuous phase by using mixed surfactants system (sorbitan monooleate (Span80), cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (DDBSs)) and peroxide initiator. PolyHIPEs was prepared by two types of mixed surfactants ratios (SPAN80, DDBSs, and CTAB; 6.3, 0.4, and 0.3 wt%)(7s) and (SPAN80, DDBSs, and CTAB; 11.3, 0.4, and 0.3 wt%)(12s). A maleimide-terminated aryl ether sulfone oligomers were used 0, 2.5, 5, 10, 20, and 30 wt% as a copolymer. The porosities and structures of materials were characterized by SEM and Brunauer-Emmett-Teller (BET) nitrogen gas adsorption. The obtained polyHIPEs showed an open cell and a secondary pore structure with surface areas of approximately 400m²/g. Compressive modulus test of the materials showed a higher modulus than for poly(DVB) polyHIPEs.

Keywords: CO₂ adsorption/ PolyHIPEs/ Polysulfone/ Mixed surfactants

4.2 Introduction

Global warming is the increasing in the average temperature of earth near the air and ocean surface. It caused by increasing concentration of green house gases; carbon dioxide methane and nitrous oxide, resulting from human activity; such as fossil fuel combustion by industrial activities and gasification processes. Therefore, it is very important to design adsorbent materials that would adsorb such gases before being liberated into the environment. Polymerization of the monomeric continuous phase of a high internal phase emulsion (HIPE) prepared highly porous crosslinked polymer materials. The monomer system which has received the most attention in polyHIPEs studies is styrene/divinylbenzene (DVB). A lot of effort was invested to determine the factors which affect the cellular structure and cell size of the resulting porous polymers, and in 1997, Neil R. C. et al. have described the production of polyHIPEs materials with high internal surface areas, employing methodologies similar to those used in porous polymer bead preparation. Scanning electron microscopy (SEM) can clearly see the foam-like morphology of open-cellular polyHIPEs materials. The open-cell polymers are characterized by an extremely low dry bulk density, less than 0.1 g cm^{-3} , which is due to complete interconnection between all neighboring cells. Their mechanical properties are similar to gas-blown polystyrene foams, although the smaller cell sizes and higher degree of cellular spherical symmetry of the emulsion-derived foams produces higher compressive strengths. However the inherent brittleness of polystyrene and the characteristic low density of polyHIPEs polymers, monolithic materials derived from styrene/DVB tend to fragment into particles rather easily under mechanical stress. Moreover, they possess lower thermo-oxidative stability and lower selective property than polysulfone. For this reason, investigations into the production of a more thermally stable and more selectivity material, involving a high-performance polymer such as polysulfone, will be entried out. The purpose of this work is to produce maleimide-terminated poly(arylene ether sulfone) PolyHIPEs, using CTAB, SPAN 80, and DDBSs as surfactants, determine the suitable condition and amounts of a surfactant for use as a carbondioxide adsorbant of the obtained polyHIPEs.

The purpose of this work is to produce maleimide-terminated poly(arylene ether sulfone) polyHIPEs, using mixed surfactants system that contains SPAN 80, DDBSs, and CTAB, determine the suitable condition and amounts of a surfactant for use as a carbon dioxide adsorbant of the obtained polyHIPEs.

4.3 Experimental

4.3.1 Materials

All chemicals were used as received. Potassium peroxodisulfate, calcium chlorohydrate dehydrated, maleic anhydride, and decyltrimethylammonium bromide were purchased from Fluka. Potassium carbonate, phosphorus pentoxide, and isopropyl alcohol were purchased from Carlo Erba. Bisphenol A 97% and dodecylbenzenesulfonic acid (DDBSs) were purchased from Aldrich. Toluene AR grade and dimethylformamide HPLC grade were purchased from Lab Scan. Divinylbenzene (DVB) and bis(4-chlorophenyl) sulfone were purchased from Merck. Span 80 was purchased from Sigma. N,N-dimethylacetamide (DMAc) 99% pure was purchased from Acros.

4.3.2 Methods

4.3.2.1 *Synthesis of 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI)*

The HPMI was synthesized according to Choi et al. In a 100 ml round bottom flask were added 30 g maleic anhydride and 30.6 g p-aminophenol and 80 ml DMF at 0 °C. A mixture of 15 g P₂O₅ in 50 ml DMF and 8 g of concentrated H₂SO₄ was added over 30 min to a round bottom flask while the flask was being stirred by a magnetic stirrer. Then the reaction mixture was stirred at 70°C for 3 h in an oil bath. After that the mixture was poured into 500 ml of de-ionized ice water and yellow precipitation was observed. The precipitate was dried under vacuum chamber for approximately 12 h and was purified by recrystallization in isopropanol. The product was in the form of yellow needle like crystals.

4.3.2.2 *Synthesis of maleimide-terminated poly(arylene ether sulfone) oligomers*

The polymerization was carried out in a 500 ml three-necked round bottom flask which was fitted with Dean Stark trap, nitrogen inlet, and

magnetic stirrer. Bis-(4-chlorophenyl)-sulfone 5.751 g was added to the reaction flask followed by bisphenol A 4.332 g and HPMI 0.4002 g, and rinsed with DMAc 65 ml to assure quantitative amount of monomers. Dried potassium carbonate 3.395 g and toluene 18 ml were added next and the reaction was refluxed at 145°C for 4 h. After the water had been removed, toluene was drawn from the Dean Stark trap the temperature increased to 155°C. The reaction proceeded for 8 h, after the solution was cooled and filtered to remove inorganic salts, then coagulated in an excess rapid stirred methanol, prior to dried under vacuum at 60°C to constant weight. The product was in the form of light grey powder.

4.3.2.3 Preparation of PolyHIPEs containing maleimide-terminated poly(arylene ether sulfone)

The cellular materials were prepared by first dissolving organic phase containing 5 ml of DVB monomer, 5 ml of toluene, required amounts of maleimide-terminated poly(arylene ether sulfone), and a mixture of nonionic, anionic, and cationic surfactants: SPAN80, DDBSs, and CTAB was added to the mixture, stirred for 10 min. While 90 ml of distilled water containing 0.2 g of potassium persulfate and 1 g of calcium chloride dehydrated were added drop-wise to the reaction flask. After all the water has been added, the emulsion was further stirred for 20 min and placed in a glass bottle. The obtained emulsions were capped and put in a convection oven at 70°C for 24 h to polymerize. After polymerization, the cellular materials were removed from the glass bottles and washed by soxhlet extraction for 6 h with isopropyl alcohol. Then the cellular materials were returned to vacuum oven to dry at 80°C for 48 h.

4.3.3 Equipments

4.3.3.1 Nuclear Magnetic Resonance (NMR)

The NMR spectra of maleimide-terminated poly(arylene ether sulfone) oligomers were obtained using ¹H-NMR and ¹³C-NMR at the Chemistry Department, Faculty of Science, Naresuan University.

4.3.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of maleimide-terminated poly(arylene ether sulfone) oligomers were obtained using Nicolet Nexus 670 FT-IR spectrometer in the

frequency range of 4000-400 cm^{-1} with 32 scans at the resolution of 2 cm^{-1} . KBr pellet technique was applied in the preparation of powder samples.

4.3.3.3 *Surface Area Analyzer (SAA)*

Nitrogen adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1MP. Samples were degassed at 100°C in a vacuum furnace prior to analysis. Surface areas were calculated using the BET method. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using adsorption of nitrogen isotherm.

4.3.3.4 *Thermalgravimetric Analysis (TGA)*

Thermalgravimetric Analysis (TGA) was performed to measure the thermal stability of the PolyHIPes. TGA of PolyHIPes was performed using a Perkin Elmer/Pyris Diamond TG/DTA instrument. Experiments were carried out under nitrogen gas atmosphere. Samples were cut into small pieces weigh about 2–5 mg. Then the samples were loaded on the platinum pan and heated to 800°C from 40°C at a heating rate of $10^{\circ}\text{C}/\text{min}$. One steps degradation was observed during testing, and the decomposition temperature was recorded corresponding to 50% decomposition of the material.

4.3.3.5 *Universal Testing Machine (LLOYD)*

A Lloyds Universal Testing Machine (Lloyds/LRX) equipped with a 500 N load cell was used to measure mechanical properties in compression. The samples were loaded at a rate of 1.27 mm/min. Samples of 25.4 mm in diameter and 25.4 mm in height were used for tested of each PolyHIPes. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached.

4.3.3.6 *Emission Scanning Electron Microscope (FE-SEM)*

Field emission scanning electron microscopy was performed on Hitachi S-4800 Model to observe surface morphology of PolyHIPes. The specimens were coated with platinum under vacuum before observation to make them electrically conductive.

4.3.3.7 *CO₂ Gas adsorption*

Study of CO₂ gas adsorption capacities of polyHIPes were carried out using a pilot gasification unit at the Chemical Technology Department,

Faculty of Science, Chulalongkorn University. Samples were cut into small pieces weigh about 1-2 g. Then the samples were loaded into sample tube 2×25 cm. CO₂ 20 ml/min and He 80 ml/min were flowed through the sample at room temperature. The residue of CO₂ was measured by a gas chromatography instruments, the column used Shimadzu 2014, flow rate 35 ml/min.

4.4 Results and Discussion

4.4.1 Characterization of maleimide-terminated poly(arylene ether sulfone) oligomers (MAPES)

The FT-IR spectra of maleimide-terminated poly(arylene ether sulfone) oligomers is showed in figure 4.1. The spectra showed bands of imide (C=O) at 3092, 3075 cm⁻¹. The adsorption bands at 1590 and 1237 cm⁻¹ indicate the presence of aryl (C-O stretching). The adsorption band at 760 cm⁻¹ shows sulfonyl (S=O stretching).

The ¹H-NMr spectra of maleimide-terminated poly(arylene ether sulfone) oligomers in chloroform solvent is shown in figure 4.2. The spectra showed bands of sulfonyl group at 7.8 ppm. The spectra bands around 7 ppm indicated the presence of para-aromatic ring and the bands around 1.6-1.8 ppm belonged to aryl group.

From these results, they were suggested that maleimide-terminated poly(arylene ether sulfone) oligomers (MAPES) were successfully produced.

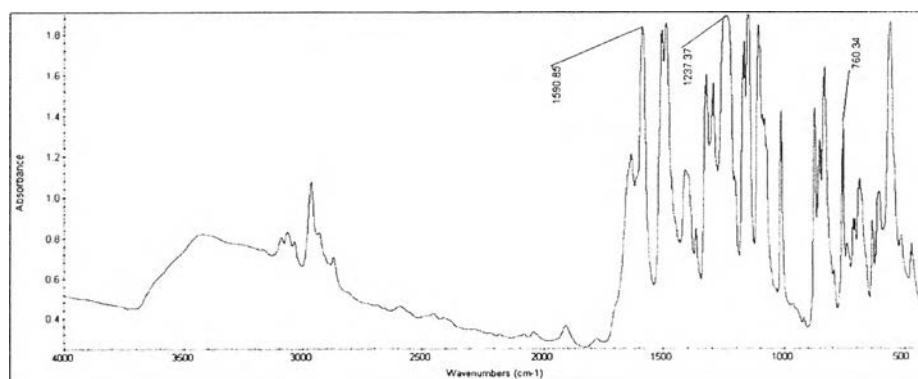


Figure 4.1 FT-IR spectra of maleimide-terminated poly(arylene ether sulfone) oligomers (MAPES).

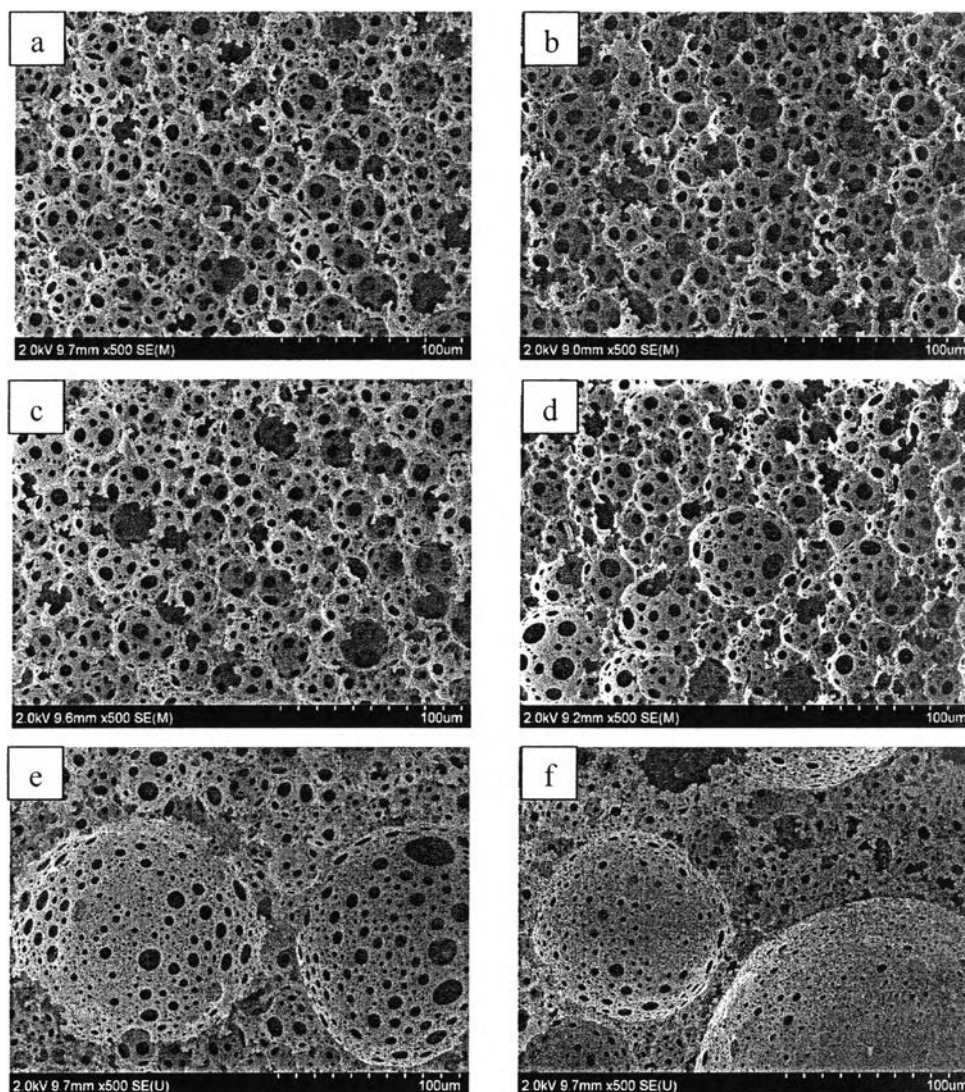


Figure 4.3 SEM micrographs of MAPES polyHIPEs materials using mixed surfactants 7s. (a) DVB, (b) DVB/2.5%wt MAPES, (c) DVB/5%wt MAPES, (d) DVB/10%wt MAPES, (e) DVB/20%wt MAPES, (f) DVB/30%wt MAPES.

The surface area results, as determined by BET analysis were found to decrease with increasing MAPES content. This results showed the number and size of large voids increased and the formation of non porous media on the polyHIPEs surface. This may due to the formation of the emulsion droplet results in the system of polyHIPEs becoming unstable. This observation was correlated with the electron micrographs and surface areas measurement.

SEM micrographs (Figure 4.4) show morphological characteristics of polyHIPEs using mixed surfactants 12s (SPAN 80, DDBSs, and CTAB; 11.3, 0.4, and 0.3 %wt) copolymerized with various MAPES content.

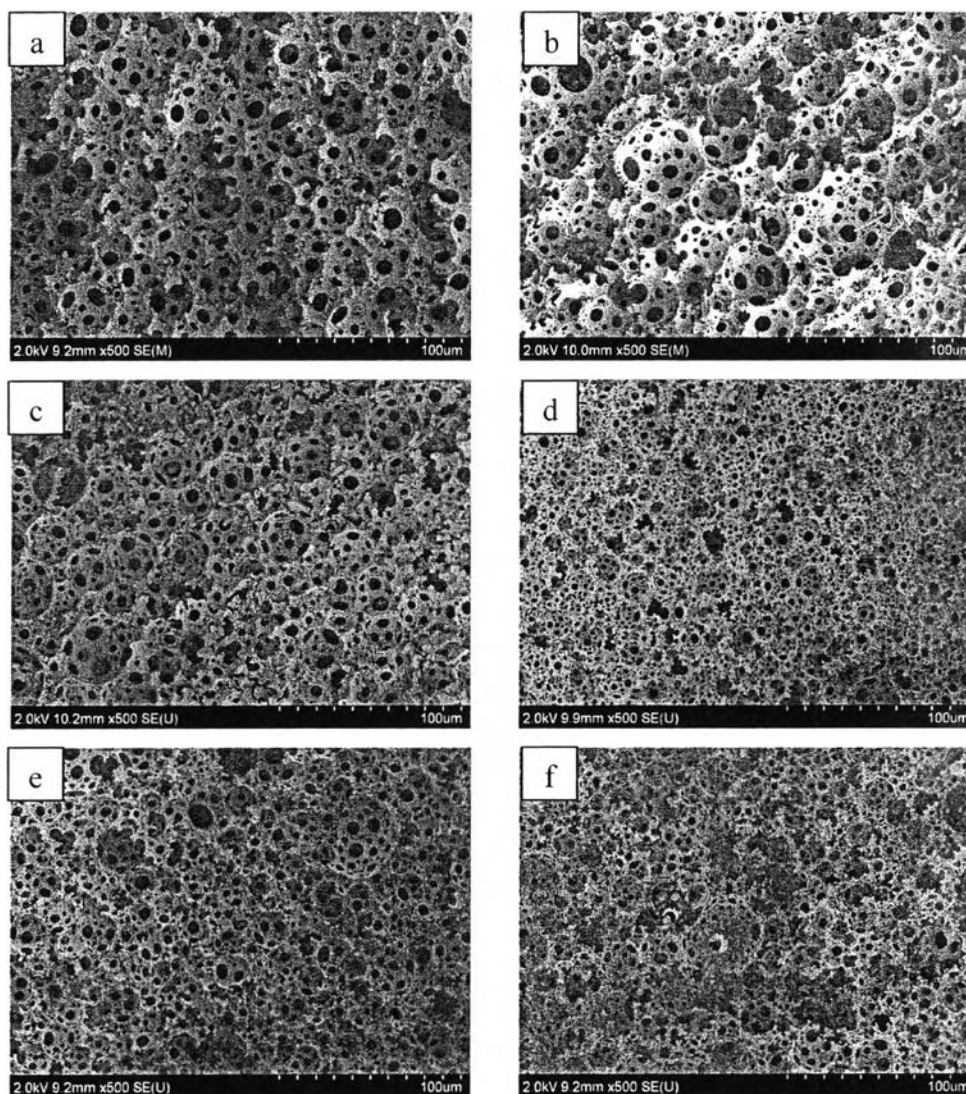


Figure 4.4 SEM micrographs of MAPES polyHIPEs materials using mixed surfactants 12s. (a) DVB, (b) DVB/2.5%wt MAPES, (c) DVB/5%wt MAPES, (d) DVB/10%wt MAPES, (e) DVB/20%wt MAPES, (f) DVB/30%wt MAPES.

The surface areas of the obtained PolyHIPEs using mixed surfactant 12s were found to decrease from 400 to 93m²/g (77%) with increasing content of MAPES (Table 4.2).

Table 4.2 Surface areas of MAPES polyHIPEs materials using mixed surfactants 12s

Sample	Surface area (m ² /g)
DVB	400.4±5
DVB+2.5 % wt MAPES	389.1±3
DVB+5 % wt MAPES	342.3±2
DVB+10 %wt MAPES	324.4±2
DVB+20 % wt MAPES	348.4±2
DVB+30 % wt MAPES	92.9±4

The surface area results, as determined by BET analysis were found to decrease with increasing MAPES content. These results showed the number voids decrease. This may due to unstable emulsion droplet induced voids collapse in the system of polyHIPEs. This observation was correlated with the electron micrograph and surface area measurement.

4.4.2.2 Thermal Properties

TGA graphs of polyHIPEs, prepared from mixed surfactant 7s and 12s copolymerized with MAPES, were carried out to measure the thermal stability of the polyHIPEs with the temperature range between 40-600°C and heating rate of 10°C/min. TGA thermogram of temperature against percent weight loss of PolyHIPEs using mixed surfactants 7s and 12s copolymerized with various MAPES content (Figure 4.5 and 4.6). The thermal decomposition temperature (Td) and residue yield (%) were listed in the Table 4.3 and 4.4.

Table 4.3 Thermal decomposition temperature (T_d) and residue yield (%) of MAPES polyHIPEs with mixed surfactants 7s

PolyHIPEs (7s)	T_d ($^{\circ}\text{C}$)	residue yield (%)
DVB	427.7	9.6
DVB/ 2.5 %wt MAPES	410.2	13.7
DVB/ 5 %wtMAPES	418.8	14.3
DVB/ 10 %wtMAPES	426.1	14.4
DVB/ 20 %wt MAPES	427.1	18.4
DVB/ 30 %wt MAPES	433.2	19.3

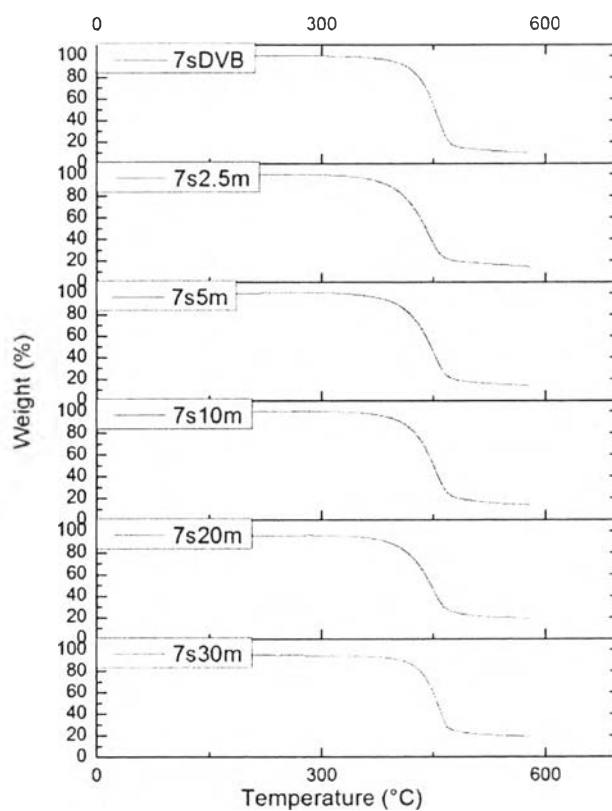


Figure 4.5 TGA thermogram of MAPES polyHIPEs with mixed surfactants 7s.

Table 4.4 Thermal decomposition temperature (T_d) and residue yield (%) of MAPES polyHIPEs with mixed surfactants 12s

PolyHIPEs (12s)	T_d (°C)	residue yield (%)
DVB	405.5	16.2
DVB/2.5 %wt MAPES	403.5	16.7
DVB/5 %wt MAPES	404.6	17.5
DVB/10 %wt MAPES	413.5	17.9
DVB/20 %wt MAPES	425.2	18.2
DVB/30 %wt MAPES	426.3	19.5

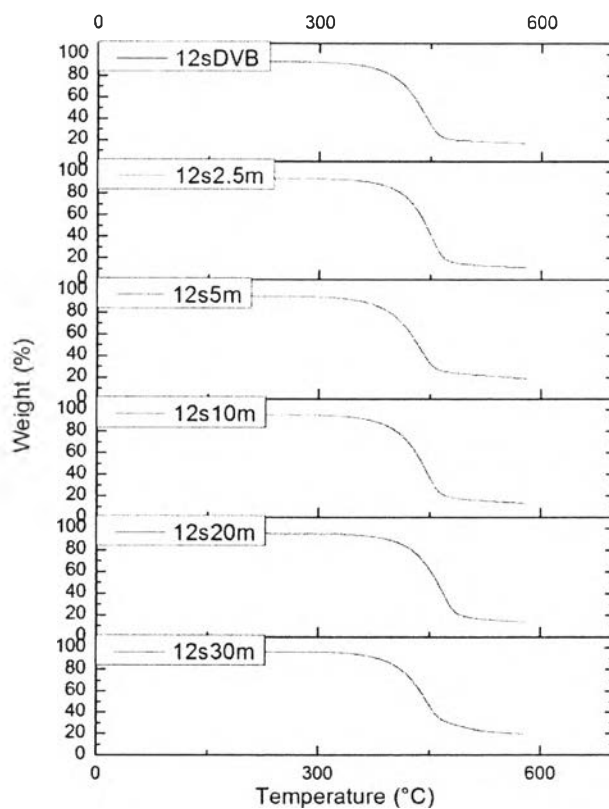


Figure 4.5 TGA thermogram of MAPES polyHIPEs with mixed surfactants 12s.

It was observed that the decomposition temperature of polyHIPEs decreased slightly at low MAPES content (2.5 %wt) and after more added MAPES 5, 10, 20, and 30 %wt the decomposition temperature shifted to a higher temperature. Residue yield of polyHIPEs copolymerized with MAPES are higher than neat polyHIPEs without MAPES. This results, indicated that the incorporation of MAPES into polyHIPEs(DVB) gives the different chemical composition of polyHIPEs(DVB) which result inconsistency decomposition temperature and higher residue yield.

4.4.2.3 Mechanical Properties

Mechanical properties of polyHIPEs, prepared from mixed surfactant 7s and 12s copolymerized with MAPES, were carried out. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached. The compressive modulus and compressive strength are shown in Table 4.5 and 4.6.

Table 4.5 Compressive test of MAPES PolyHIPEs with mixed surfactants 7s

PolyHIPEs	Compressive Modulus (MPa)	Compressive strength (MPa)
DVB	1.51±0.21	0.10±0.03
DVB/2.5% MAPES	2.77±0.16	0.15±0.04
DVB/5% MAPES	3.19±0.14	0.18±0.04
DVB/10% MAPES	3.28±0.19	0.19±0.02
DVB/20% MAPES	2.75±0.15	0.14±0.05
DVB/30% MAPES	2.18±0.23	0.12±0.03

Table 4.6 Compressive test of MAPES PolyHIPEs with mixed surfactants 12s

PolyHIPEs	Compressive Modulus (MPa)	Compressive strength (MPa)
DVB	1.65±0.22	0.10±0.05
DVB/2.5 %wt MAPES	2.06±0.19	0.12±0.06
DVB/5 %wt MAPES	2.17±0.16	0.14±0.06
DVB/10 %wt MAPES	2.21±0.16	0.14±0.02
DVB/20 %wt MAPES	1.46±0.23	0.08±0.02
DVB/30 %wt MAPES	1.25±0.21	0.07±0.01

PolyHIPEs without adding MAPES showed the compressive modulus and compressive strength of 1.51 and 0.10 MPa, respectively. PolyHIPEs copolymerized with 2.5 to 10%wt MAPES showed higher compressive modulus and compressive strength. PolyHIPEs with adding MAPES over 10 %wt MAPES have the results slightly decreased when compare to PolyHIPEs with added 10 %wt MAPES.

4.4.2.4 CO₂ Adsorption Analysis

CO₂ gas adsorption of the obtained polyHIPEs, prepared from different mixture of surfactants with different amount of MAPES content (%wt), were carried out using a pilot gasification unit at the Department of Chemical Technology, Faculty of Science, Chulalongkorn University with CO₂ flow rate of 20 ml/min and He 80 ml/min through the sample at room temperature. The CO₂ gas adsorption capacities of MAPES polyHIPEs with mixed surfactant of 7s and 12s were listed in Table 4.7 and 4.8 respectively.

Table 4.7 CO₂ gas adsorption capacities (mmol/g) of MAPES polyHIPes with mixed surfactants of 7s

Sample	CO ₂ adsorption (mmol/g)
DVB	3.22
DVB/2.5 %wt MAPES	3.32
DVB/5 %wt MAPES	3.78
DVB/10 %wt MAPES	4.12
DVB/20 %wt MAPES	4.35
DVB/30 %wt MAPES	4.32

Poly(DVB)HIPes without MAPES in mixed surfactants 7s showed CO₂ gas adsorption capacity of 3.22 mmol/g. MAPES polyHIPes with mixed surfactants 7s showed higher CO₂ gas capacities than neat poly(DVB)HIPes, increasing from 3.32 to 4.35 mmol/g and the CO₂ gas adsorption was found to remain after added MAPES over 20 %wt.

Table 4.8 CO₂ gas adsorption capacities (mmol/g) of MAPES polyHIPes with mixed surfactants of 12s

Sample	CO ₂ adsorption (mmol/g)
DVB	2.99
DVB/2.5 %wt MAPES	3.10
DVB/5 %wt MAPES	3.55
DVB/10 %wt MAPES	3.68
DVB/20 %wt MAPES	3.72
DVB/30 %wt MAPES	3.69

Poly(DVB)HIPes without MAPES in mixed surfactants 12s showed CO₂ gas adsorption capacity of 2.99 mmol/g. MAPES polyHIPes with

mixed surfactants 12s showed higher CO₂ gas capacities than neat poly(DVB)HIPES, increasing from 3.10 to 3.72 mmol/g and the CO₂ gas adsorption was found to decrease after added MAPES over 20 %wt.

Surface area and CO₂ adsorption of the obtained polyHIPES with different amount of MAPES in mixed surfactants 7s system were showed in Table 4.9. The surface areas were found to decrease about 50% with increasing content of MAPES added. From the result, indicate that when increase content of MAPES, the formation of the emulsion droplet results in the system of polyHIPES becoming unstable. On the other hand, CO₂ gas adsorption capacities were found to increase with increasing content of MAPES due to MAPES has S=O functional group which soluble with CO₂.

Table 4.9 Surface area and CO₂ adsorption of polyHIPES with different content of MAPES in mixed surfactants 7s

Sample	Surface areas (m ² /g)	CO ₂ adsorption (mmol/g)
DVB	531.9±2	3.22
DVB/2.5 %wt MAPES	514.1±4	3.32
DVB/5 %wt MAPES	453.9±1	3.78
DVB/10 %wt MAPES	400.4±2	4.12
DVB/20 %wt MAPES	342.2±3	4.35
DVB/30 %wt MAPES	265.1±5	4.32

Surface area and CO₂ adsorption of the obtained polyHIPES with different amount of MAPES in mixed surfactants 12s system were showed in Table 4.10. The surface areas were found to decrease about 80% with increasing content of MAPES added. From the result, indicate that when increase content of MAPES, the formation of the emulsion droplet results in the system of polyHIPES becoming unstable. On the other hand, CO₂ gas adsorption capacities were found to

increase with increasing content of MAPES due to MAPES has S=O functional group which soluble with CO₂.

Table 4.10 Surface area and CO₂ adsorption of polyHIPEs with different content of MAPES in mixed surfactants 12s

Sample	Surface areas (m ² /g)	CO ₂ adsorption (mmol/g)
DVB	400.4±5	2.99
DVB/2.5 %wt MAPES	389.1±3	3.10
DVB/5 %wt MAPES	342.3±2	3.55
DVB/10 %wt MAPES	324.4±2	3.68
DVB/20 %wt MAPES	348.4±2	3.72
DVB/30 %wt MAPES	92.9±4	3.69

4.5 Conclusions

PolyHIPEs porous foam was prepared successfully by using mixed ratio 6.3:0.4:0.3 (SPAN 80 : DDBSs : CTAB) (7s) and 11.3:0.4:0.3 (SPAN 80 : DDBSs : CTAB) (12s) copolymerized with MAPES(0, 2.5, 5, 10, 20, and 30 %wt). The obtained polyHIPEs were characterized for phase morphology and surface area. The surface areas of PolyHIPEs, containing MAPES 0-30% for both mixed surfactants 7s and 12s, are found to decrease with increasing MAPES content. From the result, indicate that when increase content of MAPES, the formation of the emulsion droplet results in the system of polyHIPEs becoming unstable. On the other hand, CO₂ gas adsorption capacities were found to increase with increasing content of MAPES due to MAPES has S=O functional group which soluble with CO₂. The optimum load content of MAPES that can be accepted and does not decrease mechanical properties (compressive modulus and compressive strength) and morphology is 10 %wt MAPES. The highest CO₂ adsorption capacity of the obtained polyHIPEs is 20 %wt MAPES.

4.6 References

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