



CHAPTER III

EXPERIMENTAL

3.1 The Synthesis of Styrenic Imbiber Beads

Materials:

1. Styrene monomer (Dow Chemical Co., Ltd. Thailand) was washed with 5% NaOH and then distilled at 145°C.
2. Benzoyl peroxide (97% purity) was obtained from Fluka and used as received.
3. Divinylbenzene (55% active, Dow Chemical Co., Ltd. Thailand) was used without further purification.
4. Hydroxy propyl methyl cellulose (100% HPMC; Methocel K4M, Dow Chemical Co., Ltd. Thailand) was used as received.
5. Hydroxy ethyl cellulose (90.8% HEC; Cellosize QP-100M-H, Union Carbide Corp.) was used as received.
6. Sodium bicarbonate was 97% purity and obtained from Fluka.

3.1.1 Optimum Quantity of the Crosslinking Agent

3.1.1.1 Composition

Water phase : suspending agent HPMC 0.4%
HEC 0.076%

(The 0.076% HEC concentration used was estimated from the manufacturers' technical bulletins to give a viscosity comparable to that of a 0.40% HPMC solution, so that the overall viscosity of the

suspending media was about the same.)

sodium bicarbonate	2%
(based on the resin)	
Monomer phase : styrene monomer	99.4%
benzoyl peroxide	0.3%
divinylbenzene	0.05%, 0.25%, 0.3%
Monomer phase volume fraction	0.1
Time-temperature schedule	70°C-2hr + 90°C-4hr
(The polymerization of polystyrene is generally not carried out isothermally but with stepwise rise of temperature)	
Agitation rate	185 rpm

3.1.1.2 Procedure

The solution of suspending agent was prepared and charged into the 500 ml reaction flask, which was equipped with a reflux condenser, a thermometer, nitrogen gas inlet and a top-supported mechanical stirrer (Figure 3.1). The suspending agent solution was preheated at 70°C for 20 minutes.

The initiator, benzoyl peroxide, and crosslinking agent, divinylbenzene, were dissolved in purified and distilled styrene monomer according to the composition above. Then the monomer solution was added into the reaction flask in which the suspending agent solution was agitated. The temperature was maintained constant at 70°C for 2 hr. and then was increased to 90°C for 4 hr. Therefore the polymerization was complete and seed beads of polystyrene crosslinked with

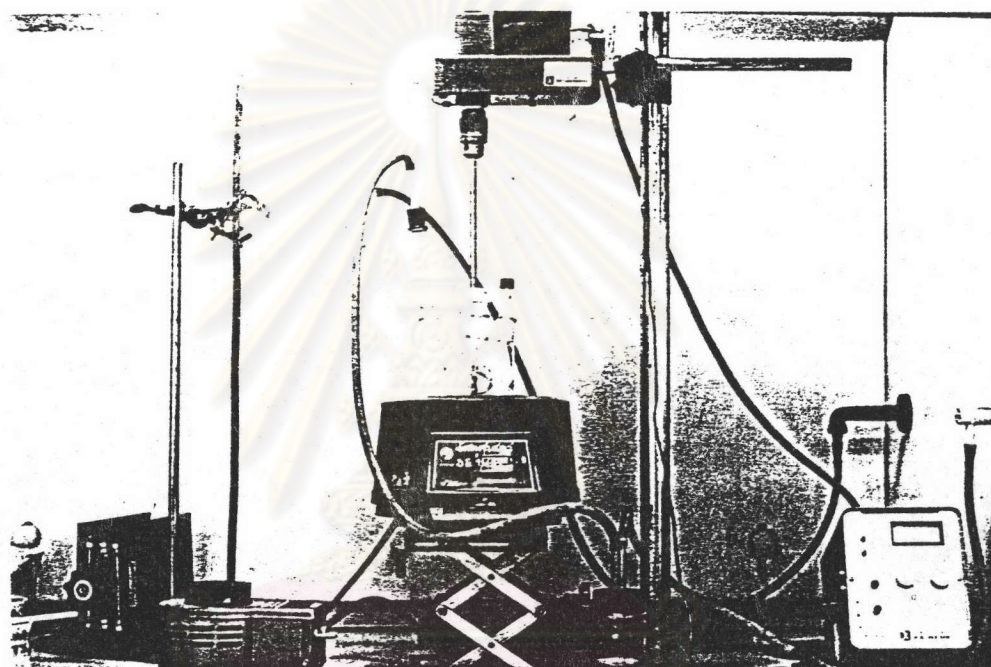


FIGURE 3.1 Suspension polymerization setup.

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divinylbenzene were received.

3.1.2 Optimum Time for Seeded Suspension

Polymerization

3.1.2.1 Composition

Water phase	: suspending agent HPMC	0.4%
	HEC	0.076%
	sodium bicarbonate	2%
	(based on the resin)	
Monomer phase	: styrene monomer	99.4%
	benzoyl peroxide	0.3%
	divinylbenzene	0.3%
Monomer phase volume fraction		0.1
Time-temperature schedule		70°C-2hr+90°C-18hr or 70°C-2hr+90°C-10hr
Agitation rate		185 rpm

3.1.2.2 Procedure

The seed beads of polystyrene crosslinked with 0.3% divinylbenzene from the last procedure were sieved into various fractions: 10, 20, 30 and 40 mesh. The sieved seed beads were then swollen in the monomer solution which was prepared in the same composition from which the seed beads were received. Swelling of seed beads was carried out at room temperature in a closed container for 24 hr. The swollen beads were strained on a sieve to separate the excess monomer and were then dispersed in the suspending medium with agitation. Polymerizations were carried out at 70°C for 2 hr and at 90°C for 18 hr or at 90°C for 10 hr.

3.1.3 Time-temperature Schedule for Suspension

Polymerization

3.1.3.1 Composition

Water phase	: suspending agent HPMC	0.4%
	HEC	0.076%
	sodium carbonate	2%
	(based on the resin)	
Monomer phase	: styrene monomer	99.4%
	benzoyl peroxide	0.3%
	divinylbenzene	0.3%
Monomer phase volume fraction		0.1
Time-temperature schedule		70°C-4hr + 90°C-2hr
Agitation rate		185. rpm

3.1.3.2 Procedure

The seed beads of polystyrene crosslinked with 0.3% divinylbenzene were produced in the same way as explained in section 3.1.1. But the polymerization time and temperature were changed to 70°C for 4 hr. and at 90°C for 2 hr.

After the seed beads were cleaned and dried, they were sieved into various fractions and then swollen in the same monomer solution for 24 hr at room temperature. The swollen beads, strained on a sieve to separate the excess monomer, were dispersed in the same suspending medium with agitation. Polymerizations were carried out at 70°C for 4 hr and at 90°C for 8 hr.

3.1.4 The Effect of Suspending Agent on Bead Size

3.1.4.1 Composition

Water phase	: suspending agent HPMC	0.8%
	sodium bicarbonate	2%
	(based on the resin)	
Monomer phase	: styrene monomer	99.4%
	benzoyl peroxide	0.3%
	divinylbenzene	0.3%
Monomer phase volume fraction		0.1
Time-temperature schedule		70°C-4hr + 90°C-2hr
Agitation rate		220 rpm

3.1.4.2 Procedure

Similar to section 3.1.3 (using only HPMC as suspending agent)

3.1.5 The Effect of Monomer Phase Volume Fraction

3.1.5.1 Composition

Water phase	: suspending agent HPMC	0.4%
	HEC	0.076%
	sodium bicarbonate	2%
	(based on the resin)	
Monomer phase	: styrene monomer	99.4%
	benzoyl peroxide	0.3%
	divinylbenzene	0.3%
Monomer phase volume fraction		0.1, 0.3, 0.5
Time-temperature schedule		70°C-4hr + 90°C-2hr
Agitation rate		220 rpm

3.1.5.2 Procedure

Similar to section 3.1.3 (Changing monomer phase volume fraction to 0.3 and 0.5)

3.2 Characterization

The polymer beads were subjected to various instrumental analyses as below.

3.2.1 Particle Size Analyses

3.2.1.1 Materials

-Sieve 10, 20, 30, 40 mesh

(mesh is the number of channels per inch)

-Beads from section 3.1.1, 3.1.3,

3.1.4

3.2.1.2 Procedure

The synthetic beads from section 3.1.1 were brought to the analyse of the particle size distribution. The wire gauze of different mesh sizes was stacked over one another varying from 10 mesh on the top to 20 mesh, 30 mesh and 40 mesh at the bottom. all the beads were first filled at the top of the stack. The smaller beads will be separated from the larger ones and passed through the upper gauze to the lower gauze for further separation, whereas the larger ones will be retained on the upper wire gauze. The results of the bead size distribution were reported in percent weight.

3.2.2. Infrared Spectroscopy: To analyse the existence of any crosslinking site inside the polymer chain.

3.2.3. Scanning Electron Microscope : To determine the porosity of the beads.

3.2.4 Brunauer, Emmett and Teller method (BET)
To determine the surface area of the bead which may, to

certain extent, relate to the ability of solvent absorption.

In addition, the characterization of pore size distribution: macro-and micro-structures, is of prime importance to determine the ability of the absorption of solvents. Due to the lack of porosimeter in Thailand, the four samples of styrenic imbiber beads of different sizes were sent to Waters, Millipore Corporation at Milford for characterization of pore volume or structure. The procedure of this characterization was described in appendix A

3.3 Solvent Sorption and Desorption by Large Imbiber Beads

3.3.1 Materials

Toluene, xylene, benzene, chloroform, carbon tetrachloride, methyl ethyl ketone, methyl methacrylate, tetrachloroethylene, 1,1,2 trichloroethane, acetone, hexane and turpentine oil.

Filter paper as the substrate in desorption experiments was Whatman No.2

3.3.2 Procedure

The large imbiber beads used in the sorption and desorption experiments were treated at 120°C in the fresh suspending medium similar to those for their syntheses in a pressure vessel for at least 8 hr. to minimize the extractable unreacted monomer.

After extracting the unreacted monomer, the

selected bead (3-5 mm.) was placed in a 50 ml beaker to immerse and swell in excess solvent. Time zero was the time when the bead was placed into the bulk solvent and the measurement of swelling kinetics started. The bead remained spherical throughout the entire process and the variation in diameter was followed by a stereomicroscope.

For desorption kinetics measurements, a fully swollen bead was placed on a piece of the filter paper substrate with an area of 9 cm² in a 50 ml. beaker. It was covered to reduce evaporation and keep out of contaminating particles. Again, the bead remained spherical and the variation of diameter was measured as a function of time.

3.4 Determination of Bead Density

The true density of the beads was measured by Auto True Denser Model MAT-5000 from Seishin Enterprise Co., Ltd. Tokyo, Japan. The principles of this measurement was described in appendix B.

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