

## CHAPTER V

### CONCLUSION AND SUGGESTION

#### 5.1 Conclusion

Suspension copolymerization is a widely-used unique process in industrial product of polymer. The advantages of suspension copolymerization include easy heat removal, low viscosity of the system, simple product recovery, low cost and easy handling. Based on the technique of suspension polymerization, we succeeded in the synthesis of styrene-divinylbenzene copolymer beads using PVA and BPO as suspending agent and initiator, respectively. Several reaction parameters affecting the properties of the copolymer beads are thoroughly investigated. The results can be summarized as followeds:

Appropriate condition for the preparation of the beads of styrene-divinylbenzene copolymer could be drawn as the following.

amount of styrene and divinylbenzene monomer (94:6)	: 100 %wt
initiator concentration (BPO)	: 0.5 %wt based on monomer phase
suspending agent concentration (PVA)	: 0.1 %wt based on monomer phase
reaction temperature	: 70°C
reaction time	: 10 h
agitation rate	: 270 rpm
weight fraction of monomer phase	: 0.1
diluent composition (toluene:heptane)	: 60:40

At the weight fraction of monomer phase is one of the unique characteristics of suspension polymerization, increasing the weight fraction of the dispersed phase (water), the average particle size shifted towards the large particle size. The most appropriate weight fraction of the monomer phase in this study was of 0.1. The weight fraction of monomer phase more than the critical point of 0.1 the copolymer beads coalesced.

The polymerization carried out in the stirred glass reactor at different agitation rates resulted in different particle sizes. The higher the rate, the smaller the resulting particles. However, when the rate of agitation was increased up to 300 rpm, the broad size distribution of the beads was obtained. Therefore, the appropriate agitation rate for this work was of 270 rpm.

The temperature is one of the main parameters affecting the properties of copolymer beads. Increasing reaction temperature results in a declining of the swelling of copolymer beads. The appropriate temperature was 70 °C.

The length of reaction time during suspension copolymerization influences the absorption property of the synthetic copolymer beads. The copolymer beads which took too long a polymerization time would deform after excessive swelling due to too the great crosslinking density that rendering the beads to become hard and brittle. The most appropriate time for the suspension polymerization in this study was of 10 hours.

Divinylbenzene was used as the crosslinking agent in the preparation of the styrenic copolymer beads. The crosslinking agent helps stabilize and maintain the dimension of the copolymer beads during absorption and desorption of the solvents. However, the large amount of the crosslinking agent made the bead rather rigid and

then decreased its absorption property. The most appropriate amount of divinylbenzene in this work was of 6 %wt.

In suspension polymerization, the stabilization depends concertedly not only on the action of agitation in the reaction system but also on the protection ability of the stabilizer or suspending agent. The particle size decreased as the concentration of suspending agent increased. The copolymer droplets were coalesced when the suspending agent concentration was less than 0.1 %wt.

The concentration of peroxide initiator of 0.1 – 2.0 %wt of the monomer phase, and the polymerization temperature at 70 °C were the suitable condition for the appropriate conversion. To obtain a suitable conversion which might be neither too low nor too high to limit the crosslinking sites was to produce the copolymer network with a maximum swelling property. In this study, the copolymer beads needed the appropriate initiator concentration of 0.5 %wt based on monomer phase.

The mixed diluent between a good solvent (toluene) and a poor solvent (heptane) is one of the key components to control the porous structure of the copolymer beads. The appropriate diluent composition (Tol:Hep) in this work was of 60:40 %wt.

The average particle sizes of the copolymer beads, determined by sieve analysis, were in the range of 0.82 – 1.49 mm.

The densities of the synthetic copolymer beads, determined by the liquid displacement technique, were in the range of 0.9375 – 1.0581 g/cm<sup>3</sup>. These copolymer beads can naturally float on a water surface.

The styrene-divinylbenzene copolymer beads with Tgs in the range of 99 – 129 °C were obtained using different DVB contents. The results indicated that the variation of toluene/heptane ratio insignificantly affect Tgs of the copolymer beads. Likewise, the terpolymer beads with Tgs in the range of 42 – 107 °C were achieved adjusting the suitable ratio of styrene and the third comonomer of *n*-butyl acrylate, or 2-ethyl hexyl acrylate in the monomer feed. The higher composition of the third comonomer resulted in a significant decrease in Tg values.

The solubility parameters of the resulting copolymer beads prepared by varying the third comonomer, *n*-butyl acrylate or 2-ethyl hexyl acrylate, estimated by swelling experiments were in the range of 18.2 – 19.0 (MPa)<sup>1/2</sup>.

As for the absorption-desorption kinetics and diffusion coefficient of the copolymer beads in toluene-heptane solution [the toluene volume fraction ( $z$ ) = 0.5], the initial stage of absorption with a high slope was of about 30 min and the swollen beads reached a stationary state in equilibrium with the surrounding solvent within 60 min. The diffusion coefficient range of copolymers prepared varying the third comonomer, *n*-butyl acrylate, or 2-ethyl hexyl acrylate, was in the range of  $6.40 \times 10^{-6}$  –  $1.52 \times 10^{-5}$  cm<sup>2</sup>/sec. When a swollen bead was placed on the filter paper, the solvent diffused into the filter paper immediately. The initial stage of desorption was of about 10 min, and the swollen bead lost all the retained solvent within 40 min after the start of desorption process. The copolymer beads could be used to absorb and desorb toluene-heptane solution for many cycles (up to at least 3 cycles). The absorption and desorption behavior of the second and third cycles were also the same as that of the first cycle. The polymer beads were also used to absorb many mixed

solvents on the water surface. The emulsified water in the mixed solvent increased the weight of absorbed mixed solvent. The polymer beads can absorb the organic solvents having the solubility parameters of  $14.9 - 20.9 \text{ (MPa)}^{1/2}$ . Increasing the number of carbon atoms of acrylated vinyl monomer from *n*-butyl acrylate ( $C_4$ ) to 2-ethyl hexyl acrylate ( $C_6$ ) incorporated in the styrene-divinylbenzene copolymer beads enhance the absorption of the aliphatic hydrocarbon solvents of hexane, heptane, and cyclohexane. This result could be explained by the solubility parameter.

The surface morphology of the resulting copolymer beads was investigated by SEM. The SEM micrographs revealed that the DVB contents and diluent compositions had a strong influence on the surface morphology. At low DVB contents and high solvating power, or a low heptane fraction, the copolymers obtained were of gel-type; on the other hand, the porous-type copolymers were obtained at high DVB contents and low solvating power, or a high heptane fraction.

The effect of diluent content between the good solvent (toluene) and the poor solvent (heptane) on the pore properties, average pore diameter, surface area, and pore volume of the resulting copolymer beads by the mercury porosimeter were  $0.0133 - 0.0212 \mu\text{m}$ ,  $17.466 - 44.057 \text{ m}^2/\text{g}$  and  $0.0581 - 0.2337 \text{ cm}^3/\text{g}$ , respectively.

## 5.2 Suggestions for Future Work

Synthesis of styrenic copolymer beads for absorption-desorption of organic solvent and spilled oil by suspension copolymerization would be further studied as follows:-

- a) Using the other monomers and various monomer compositions in order to obtain the copolymer beads which can absorb the wider range of solvents and oil.
- b) Using other type of suspending agent which may produce large monomer droplets during polymerization.
- c) Changing the other mixed diluent or using the linear polymer as the porogen, such as linear polystyrene, in the monomer phase during the polymerization to improve the porous structure of the copolymer beads.
- d) Other kinds of solvent mixtures and various solvent compositions should be used to characterize the absorption ability and spectrum.