CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Suspension Polymerization

Suspension polymerization is a system in which monomer(s) is(are) suspended as the discontinuous phase of droplets in a continuous phase and polymerized, one or more water-insoluble monomers containing oil-soluble initiator(s) is(are) dispersed in the continuous aqueous phase by a combination of strong stirring and the use of small amounts of suspending agents(stabilizers). Suitable conditions of mechanical agitation are maintained while the monomer droplets are slowly converted from a highly mobile liquid state, through a sticky syrup-like dispersion (conversion 20-60%), to hard solid polymer particles (conversion > 70%). The stabilizers hinder the coalescence of the monomer droplets first, and later stabilize the polymer beads whose tendency to agglomerate may become critical when the polymerization has advanced to the point where the polymer beads become sticky.

The most important issue in the practical operation of suspension polymerization is the control of the final particle size distribution. Suspension polymer particle diameters range usually between 50 and 2000 μm, the exact size depending on the monomer type, the concentration of stabilizer, and the agitation conditions in the reactor. These particles are much larger than those formed in emulsion polymerization (20-1000 nm). The particle morphology is an important characteristic for the application of the polymer product, particularly in the case of expandable polystyrene and ion-exchange resins [2].

2.1.1 Bead (or Pearl) Suspension Polymerization.

The preparation of bead (or pearl) by suspension polymerization is obtained as particle diameter in the range of 50-200 μm. This process gives particle diameter much larger than other polymerizations, which can produce particle diameter upto 400 μm. So it is called bead or pearl. In bead (or pearl) suspension polymerization, the monomer droplets pass through a viscous syrupy state and finally transform to solid clear spheres (beads).

2.1.2 Characteristics of Suspension Polymerization Method

A number of important effects for polymer beads made by suspension polymerization are:

1. The weight ratio of the continuous water phase to the discontinuous monomer phase varies from 1:1 to 4:1 in process. Because the bulk viscosity of the slurry is near that of water during most of the polymerization. The low bulk fluid viscosity allows good mixing of the reactor content at modest energy inputs and can improve heat transfer.

2. Suspension droplets are not thermodynamically stable, and their coalescence is controlled by balancing the agitation system and the suspending agents.

3. The medium of suspension polymerization is water because it has both a high heat capacity and a high thermal conductivity for removing heat from polymerizing droplets.

2.2 Comparison of Suspension Polymerization with Other Polymerization Processes.

Suspension polymerization, one of the free radical polymerization, has advantages and disadvantages compared with bulk, solution and emulsion polymerizations, as follows:

2.2.1 Advantages

1. Easy heat removal and temperature control.

2. Low dispersion viscosity.

3. Low levels of impurities in the polymer product (compared with those of the emulsion polymerization).

4. Low separation costs (compared with emulsion polymerization)

5. Final product is in a particle form.
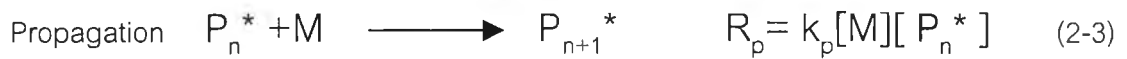
2.2.2 Disadvantages

1. Lower productivity for the same reactor capacity (compared to bulk).

2. Waste water problems.

3. Polymer builds up on the reactor wall, baffles, agitators, and other surfaces.

4. No commercial continuous process operable yet.

5. Difficult to produce homogeneous copolymer composition during batch suspension polymerization.
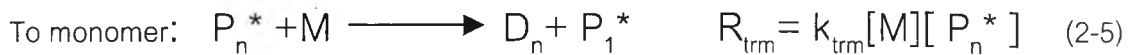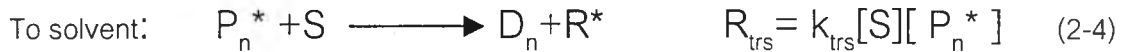
2.3 Kinetic Modeling

In general, the time-conversion curves, heat of polymerization, and the dependence of the initial polymerization rate upon initiator concentration in suspension polymerizations are in good agreement with bulk polymerization kinetics. Particle size,

type and concentration of stabilizer, and agitation conditions seem to have no influence on the polymerization rate in a batch suspension homo-polymerization process. Hence, mass transfer phenomena between the two phases do not significantly affect the overall process [3].
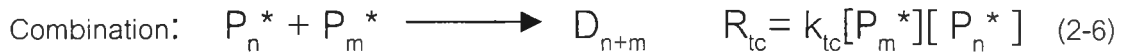
The basic kinetic scheme for a free radical polymerization.

Initiation $\qquad$ I $\longrightarrow$ 2R* $\qquad$ $R_d = 2fk_d I$ $\qquad$ (2-1)

$\qquad$ R* + M $\xrightarrow{\text{(fast)}}$ P_1^* $\qquad$ $R_i = k_i[M][R^*]$ $\qquad$ (2-2)

Propagation $\quad$ $P_n^* + M \longrightarrow P_{n+1}^*$ $\qquad$ $R_p = k_p[M][P_n^*]$ $\quad$ (2-3)

Chain transfer

To solvent: $\quad$ $P_n^* + S \longrightarrow D_n + R^*$ $\qquad$ $R_{trs} = k_{trs}[S][P_n^*]$ $\quad$ (2-4)

To monomer: $\quad$ $P_n^* + M \longrightarrow D_n + P_1^*$ $\qquad$ $R_{trm} = k_{trm}[M][P_n^*]$ $\quad$ (2-5)

Termination

Combination: $\quad$ $P_n^* + P_m^* \longrightarrow D_{n+m}$ $\qquad$ $R_{tc} = k_{tc}[P_m^*][P_n^*]$ $\quad$ (2-6)

Disproportionation: $P_n^* + P_m^* \longrightarrow D_n + D_m$ $\quad$ $R_{td} = k_{td}[P_m^*][P_n^*]$ $\quad$ (2-7)

where :

I is initiator concentration

R* is the radical produced by dissociation of the initiator

M is monomer concentration

P_n^* is a growing polymer chain having n repeating units

D_n is a polymer with n repeating units

$k_d, k_i, k_p, k_{trs}, k_{trm}, k_{tc}, k_{td}$ are rate of constants of decomposition, initiation, propagation, chain transfer to solvent, chain transfer to monomer, termination by coupling and termination by disproportionation, respectively.

2.4 Particle Formation and Properties

A principal advantage of a suspension polymerization over an emulsion polymerization is that the formation of a "uniform" suspension of monomer droplets in the aqueous phase and the reduction of coalescence of the droplets during polymerization.

The monomer must be relatively insoluble in water for the droplets to form. A typical water-insoluble organic monomer has a lower surface tension than water. When such a monomer is mixed continuously as a dispersed phase in a continuous phase of water with no surfactants present, an unstable dispersion forms due to the continuous breakup and coalescence of monomer droplets. If the agitation stops, the monomer-water system will separate into its two phase. Particle coalescence is not prevented but it is controlled by combination of surfactant and agitation-system design.

The process of particle formation can be divided into three stages.

In the first stage, a liquid-liquid dispersion exists; the liquid monomer is dispersed into small droplets, stabilized by a combined action of the rotating stirrer and the suspending agents.

In the second stage, a break-up coalescence and dynamic equilibrium of the monomer-polymer droplets seem to determine the final particle size. The viscosity of the droplets increases with increasing conversion. The droplets break-up by the impeller shear stress and recoalesce back after collision with each other.

In the third stage, the polymer particles are solid and they do not stick any more. After this point, which is called particle identity point (PIP), the viscosity of polymer particles is too high, so they cannot be broken-up, and their diameter remains constant.

2.5 Suspending Agents

The suspending agents(stabilizers) are key factors in suspension polymerization, which affect particle size and shape, help establish the initial monomer droplet size distribution, control droplet coalescence, and reduce particle agglomeration.

Types of suspending agents:

1. Water-soluble organic polymers: natural polymers, modified natural polymers, and synthetic polymers.

2. Insoluble finely divided inorganic powders: Mg, Ca, Al salts or even silica.

3. Mixed stabilizers: Organic polymers with inorganic powders or inorganic powders with surfactants.

Table 2.1 Industrial stabilizers used in suspension polymerization:

Polymer suggested	Suspending agent
1. Poly(vinyl chloride) and copolymers	Gelatin, hydropropyl methyl cellulose , methyl cellulose, poly(vinyl alcohol).

2. Styrene resins:
  - Expandable Polystyrene (EPS)
  - High Impact Polystyrene (HIPS)
  -General Purpose Polystyrene (GPPS)
	Gelatin, methyl cellulose, poly(acrylic acid) and its salts, starch, poly(vinyl alcohol), poly(vinyl pyrrolidone), sulfonated polystyrene, alkaline earth phosphates, carbonates and/or silicates, magnesium silicates, hydroxylethyl cellulose, zinc oxide, $Mg(OH)_2$, Methyl methacrylate copolymer, hydroxyapatite, sodium dodecylbenzene sulfonate.

3. Acrylonitrile-Butadiene-Styrene (ABS)	Acrylic acid-2-ethylhexyl acrylate copolymer, poly(vinyl alcohol), carboxymethylcellulose, water-soluble acrylic polymers.

Table 2.1 (Continued)

Polymer suggested	Suspending agent
4. Styrene Acrylonitrile Copolymer (SAN)	Acrylic acid-2-ethylhexyl acrylate (90:10), hydroxyapatite, sodium dodecylbenzene sulfonate.
5. Acrylic resins	Glycerol, glycols, polyglycols, $MgCO_3$, sodium alkyl sulfonate.
6. Polyvinyl acetate	Hydroxyethyl cellulose, poly(vinyl alcohol).

2.5.1 Role of Stabilizer.

The importance of various interfacial tensions in predicting the morphology obtained and the role of stabilizer can play in affecting the equilibrium particle morphology. When a monomer is mixed continuously as a dispersed phase in a continuous phase of water in which no stabilizer is present, lower case unstable dispersion forms due to the continuous break up and coalescence of monomer droplets. If the agitation stops, the monomer-water system will separate into their two phases. The polymeric stabilizer is dissolved in aqueous phase. It was adsorbed on the monomer particle surface, and the particles then change gradually into polymer particles. While the other parts of stabilizer are oriented outwards from the interphase into the water, lower case decreased the interfacial tension between the monomer droplet and water to promote the dispersion of droplets. On the other hand, the stabilizer is being spread over the particle surface to produce a thin layer on the surface of the monomer droplets which prevents coalescence when collision occurs between the particle droplets in a turbulent flow. In the situation, the polymer particles do not coalesce if the repulsive forces prevail over the attractive ones. Collisions of these stable particles are accompanied only by overlapping the osmotic pressure increase, which

gradually separates the particles one from the others. The rate of separation of suspension particle, whose surface layer mutually overlaps after collision is not interactions between the stabilizer molecules and polymer and monomer [4].

2.6 Core-Shell Particle Structure

The core-shell particles are usually prepared by a series of consecutive suspension polymerization sequences with different monomer types, where the second stage monomer is polymerized in the presence of seed particles. The seed particles may be prepared in a separate step, or formed in situ during the suspension polymerization. The resulting particles are commonly referred to as "core-shell" particle, implying a particle structure with the initially polymerized polymer located in the centre of the particle and the later formed polymer(s) becoming incorporated into the outer shell layer.

The formation of an unique multi-layered heterogeneous structure can be expected. Depending on the polymerization process variables, seeded suspension polymerization reaction can produce structured particles, which exhibit a wide variety of particle morphologies such as the familiar core-shell, hemispherical particles with various fragmented inclusions, or "inverted" core-shell particle with the second stage polymer becoming incoporated at the centre of the particles and the seed polymer found on the periphery of the composite particle, shown in Figure 2.1 [5].
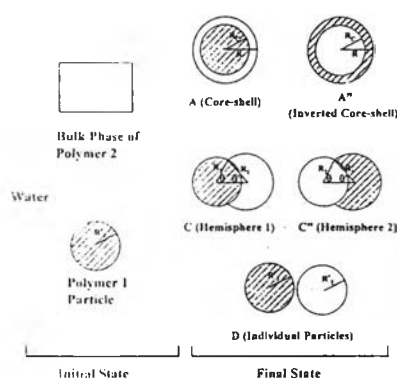

Figure 2.1 Core-Shell particle structure

2.6.1 Preparation of Core-Shell Particle Structure

2.6.1.1 Seeded Suspension Polymerization

Seeded polymerization is a potential technique for preparing core-shell polymeric particles which is composed of 2 steps.

1. Preparation of the seed particles by suspension polymerization of the first monomer.

2. Addition of the second monomer to the seed particle from stage 1 by seeded suspension polymerization for a formation of the shell layer onto the seed particle.

This process was performed in three ways.

(a). The equilibrium swelling process, in which the second monomer was allowed to swell the seed particle until the swelling equilibrium is attained. Then the polymerization is performed.

(b). The semi batch process, in which the second monomer was added continuously to the reaction flask from a microfeeder.

(c). The batch process, in which the monomer was added to the reaction flask just before the seeded suspension polymerization was initiated [6].

2.6.1.2 One-Stage Suspension Polymerization

The formation of core-shell particle can be run by one-stage suspension polymerization. The system of reaction is composed of two monomers, a medium, an initiator, a stabilizer, which was occasionally agitated at a high speed in the same time before polymerization was initiated.

The core-shell is achieved when two monomers are assumed to differ in the reactivity ratio and hydrophilic property.

2.6.2 Important Polymerization Parameters in Controlling Particle Morphology

2.6.2.1 Effect of Monomer Addition

The factor affecting the particle morphology of incompatible polymer systems is kinetics of phase separation. The attainment of true core-shell particle morphology can be made more likely in those situations when the thermodynamically-favoured morphology is not a core-shell structure by controlling the kinetics of the morphological development.

1. Batch Mode of Monomer Addition

All monomers are added to the first-stage particles at the start of the polymerization. The relatively low viscosity of the polymerization is achieved. This enhances the polymer chain mobility, and therefore the migration of the two immiscible polymers in different domains occurs.

2.Semi-Continuous Monomer Addition

The second-stage monomer is added continuously to the seeded polymer at a controlled feed rate. The monomer concentration in the particles can be maintained at a minimum value. The extremely high local viscosity creates a kinetic barrier towards polymer chain diffusion and decreases the degree of phase separation. The desired polymer composite, with a particular purpose, is obtained in which particle morphology thermodynamically non-equilibrium ones are desirable.

2.6.2.2 Effect of Initiator Concentration

At a high initiator concentration, branching is favored due to the increasing radical flux. The polydispersity Index (PDI) of polymer particles is broad [7], because of the increase of the latex particle size with higher initiator concentration.

2.6.2.3 Effect of Polymer Crosslinker

Another method which is used to increase the kinetic barrier to phase inversion and create more stable non-equilibrium morphologies is to introduce crosslinking in one or in both of the polymer phase. Generally, crosslinking of the seed (core) particle would result in an enhancement of phase separation. In most cases hemispherical structures with multiple surface domains would be obtained. By crosslinking at least one of the polymer phases, the chain mobility is limited, which restricts the composite particle to the configuration that corresponds to its minimum free energy.

2.6.2.4 Effect of Chain Transfer Agent

The presence of chain transfer agents during the second-stage polymerization produces a decrease in the molar mass of the shell polymer, which will result in more chain mobility and freedom to achieve the equilibrium morphology, even under conditions where kinetically controlled particle morphologies (i.e. semi-continuous monomer addition) would normally dominate.

2.7 Absorption – Desorption Kinetics

2.7.1 Absorption Kinetics

When a piece of polymer is added to a solvent, the polymer chains interact with the molecules of the solvent, which is absorbed by the polymer. As the contact with the solvent continues, these chains gradually extend and relax. Then they may disentangle, diffuse into the bulk of the solvent, and become dissolve [8]. If the polymer is crosslinked, it would remain linked to each other through chemical bonds. The polymer may swell but it cannot dissolve in the solvent. The swelling of these materials is determined by the solvent properties of the liquid for the polymer and the degree of the crosslinking. The positive entropy of mixing of the polymer and the solvent enhances swelling. The heat of mixing may enhance (if negative) or retard (if positive) the swelling. The tension setup in the polymer subchains resists the swelling. A "good"

solvent will give a high degree of swelling. A lightly crosslinked polymer will give a high degree of swelling, and a heavily crosslinked polymer will give a small degree of swelling.

Characterization of the swelling of spherical gels in liquids as a relaxation process [9]. They define the diffusion coefficient of the gel in the liquid by the following equation: (2-9)

$$D = [(4U/3) + K]/f \qquad (2\text{-}8)$$

U = Shear modulus of the polymer network alone,

K = Bulk modulus of the polymer network alone,

f = Friction coefficient between the network and the fluid medium,

D = Diffusion coefficient of solvent.

The measurement of the difference between the size at time t and at a saturation swelling can bring data to calculate τ from the following equation.

$$\ln (\Delta a_t / \Delta a_0) = \text{const.} - t/\tau \text{ (for } t/\tau > 0.25) \qquad (2\text{-}9)$$

where τ = characteristic swelling time = a^2/D (2-10)

    t = time

Δa_t = the difference between the size (radius) at time t and that at the saturation swelling

Δa_0 = the total change in radius throughout the entire swelling process

    a = the final radius of the fully swollen gel

The characteristic swelling time (τ; Characteristic Swelling Time) can be obtained from the slope of the ln $(\Delta a_t / \Delta a_0)$ – time plot.

2.7.2 Desorption Kinetics

By bringing the swollen gel into contact with a substrate and separating it from the bulk of the swelling liquid, the imbibed solvent may be released. If the substrate competes favorably against the solvent, the desorption will be effective. If the substrate competes poorly, the desorption will be incomplete. A rapid sorption by the substrate makes the desorption from the bead rapid. A slow sorption by the substrate makes the desorption slow. The diffusion of the solvent into the substrate has been shown to follow the Rideal-Washburn equation [10], which describes the penetration of a liquid into capillary pores:

$$I^2 = r\,t\,\eta\ \cos\theta/2\ =\ Kt\cos\theta/2 \tag{2-11}$$

where
I = the depth of penetration

r = the radius of the cylindrical capillaries

t = time of penetration

θ = contact angle of the liquid on the capillary walls

η = the viscosity of the liquid

K = the effective radius of non-cylindrical capillary pores including a tortuousity factor

2.8 Literatuer Review

Grancio and Williams [11,12] proposed the non-uniform "core-shell" theory of particle growth in seeded emulsion polymerization of styrene onto polystyrene seed particle. The emulsion polymerization of styrene assumed that the particles were swollen homogeneously with the monomer. There was no concentration gradient from center of the particle to its surface, because styrene monomer is miscible with polystyrene in all proportions.

Okubo et al. [13] synthesized the micron-sized monodispersed PMMA/PS particles at PMMA/PS = 2/1 wt ratio, by seeded dispersion polymerization. The particle morphology in this seeded dispersion polymerization system was controlled kinetically so that it consisted of PMMA-core and PS-shell. In other words, seeded dispersion polymerization technique has an advantage to produce core/shell polymer particles in which polymer layers accumulate in their order of production, regardless of the hydrophobicity of polymers forming core and shell, namely, even if the morphology so produced is unstable thermodynamically.

Cho and Lee [14] studied the morphology of composite latex particles, prepared by PMMA-seeded emulsion polymerization of styrene that could be controlled by various polymerization reaction parameters, i.e., the decomposition rate of $K_2S_2O_8$ remained unchangeable in the pH range of 3-12. In this pH range, the particle morphology was not affected. The anchoring effect was exhibited by the terminal functional groups originated from the ionic initiators affected significantly the particle morphology. The viscosity of polymerization loci controlled the mobility of polymer molecules. Therefore, at the PS/PMMA ratio of 3.0, the PS is shelled and the PMMA is core.

Kiatkamjornwong and Asawaworarith [15] synthesized poly(styrene-co-divinylbenzene) using suspension polymerization of the mixture of 0.4 % hydroxy propyl methyl cellulose and 0.076 % hydroxy ethyl cellulose as suspending agents and benzoyl peroxide as an initiator. The time schedule for polymerization was $70^{\circ}C$ - 4 hr and $90^{\circ}C$ - 2 hr. and seeded suspension polymerization program was $70^{\circ}C$ - 10 hr and $90^{\circ}C$ - 2 hr. The properties of copolymer beads are the specific surface area of $0.1\text{-}0.8 \times 10^3$ $m^2 g^{-1}$ and density 1.05 kg m^{-3}, The maximum absorption of 13 times its own dimension and the complete desorption time of the absorbed toluene at 23 hr.

Kiatkamjornwong et al. [16] studied the effect of the styrene-divinylbenzene copolymer beads prepared by the conventional and seeded suspension polymerization in various quantities of diluents, toluene and n-heptane. The optimum conditions for the polymerization were as follows: the suspending agents were the mixture of 2.53 % hydroxy propyl methyl cellulose and 1.32 % hydroxy ethyl cellulose; hydroquinone 0.16 %;

the monomer phase volume fraction was 0.075; the amount of crosslinking monomer was 1 %: temperature and time schedules for the conventional polymerization were 70°C - 4 hr and 90°C - 3 hr, and seeded polymerization were 70°C - 4 hr and 90°C - 2 hr. The synthetic beads had the following properties: pore volume 0.12 m^3kg^{-1}, specific surface area 139.87 m^2g^{-1}, density 0.9667 kg m^{-3}, and swelling ratio in toluene 16.4 within 50 min.

Kangwansupamonkon [17] synthesized styrene-divinylbenzene copolymer beads by suspension polymerization. The optimum conditions for the polymerization were found as follows: the suspending agents 0.1 %w/w, initiator agent 0.5 %w/w, the monomer phase weight fraction 0.1, crosslinking agent of the divinylbenzene 6 % w/w and the mixture of toluene and heptane 60:40. The reaction time and temperature were 10 hr. and 70°C, respectively. The synthetic beads had the following properties: average particle sizes were in the range of 0.82 – 1.49 mm., average diameter (1.33 – 2.12) mm., pore volume 5.81 $\times 10^{-2}$ – 2.34 $\times 10^{-1}$ cm^3g^{-1}, surface area 17.466 – 44.057 m^2g^{-1}, density (0.9375–1.0581) $\times 10^{-3}$ kg m^{-3}, and the swelling ratio in the range of 4.2 – 12.3 times in toluene.