

CHAPTER 1

INTRODUCTION

Emulsion polymerization is one of four principle types of polymerization processes, namely, bulk, solution, suspension and emulsion polymerization. It has become a more attractive technique for industrial production of polymeric materials because it offers some unique advantages over other polymerization techniques.

Emulsion polymerization is a dominant process for poly(vinyl acetate), polychloroprene, various polyacrylate, poly(vinyl chloride), acrylonitrile-butadiene-styrene copolymer, poly(methyl methacrylate), poly(vinylidene chloride) and polystyrene.

Emulsion polymer can be used directly as latex products such as latex paints, adhesives, coatings, floor coverings or indirect used as bulk polymeric resins by removing polymers from the latex via coagulation and dewatering, Hamielec and Friis(1975), Odian(1981).

1.1 Recipe components

An emulsion polymerization recipe component comprises of four essential ingredients, dispersion medium, monomer, initiator and emulsifier.

1 Dispersion medium.

In general, the dispersion medium is water, in some low temperature polymerization, mixture of water and methanol is sometimes used. Water in emulsion polymerization must be deionized water in order to eliminate the effect of other ions on initiation process and on emulsifier functions. Anti-freeze additives must be added to the reaction operated at temperature lower than 0 °C. Organic electrolytes such as ethylene glycol, methyl alcohol and monoalkyl ester of ethylene glycol are also used as an anti-freeze additive.

2 Monomer.

In emulsion polymerization, monomers form dispersed particles which suspended in dispersion medium. All dispersed monomer droplets act as storehouse of monomer. Monomer must be insoluble or only slightly soluble in dispersion medium. Before the polymerization reaction begins, monomers are found in three different loci. The major part, more than 95 %, is present as 1-10 μ in diameter monomer droplets. A small amount is solubilized in micelle. Finally, a very small amount of monomer is present as a solute in the dispersion medium. The distribution of monomer in these three loci depends on the nature of monomer, temperature, emulsifier concentration and emulsifier type.

3 Initiator.

Azo and diazo compounds which are soluble in water and monomer or in both phases can be used as initiators. The most widely used initiators in emulsion polymerization are water-soluble peroxide, partially water-soluble hydroperoxide and redox catalyst system.

Initiators in emulsion system are divided into four groups with respect to their nature.

i Water soluble initiators such as persulfates, perborate and hydrogen peroxide. In this group, free radicals are formed only in the aqueous phase. Free radicals are either directly captured by micelles and monomer-swollen polymer particles or convert to oligomeric radicals after having added molecules of dissolved monomers.

ii Initiators soluble in the water and monomer phases such as 1,1-diphenylethane hydroperoxide, tert-butyl hydroperoxide, cumyl hydroperoxide. Initiators of this group are distributed in different phase and different rate of initiation in each phase.

iii Water insoluble initiators such as lauryl peroxide, benzoyl peroxide and azobisisobutyronitrile. Free radicals of this type are generated in the monomer droplets, micelles or monomer-swollen polymer particles.

iv Redox initiator system which the reducing component or its reaction product is the emulsifier. The characteristic of this type is the fact that initiation occurs in the zone of surface layer which influences the polymerization characteristics and polymer properties.

4 Emulsifier.

The emulsifier molecule consists of two parts, hydrophilic and hydrophobic ends. All emulsifiers can be divided into two groups.

1 Semicolloidal emulsifiers, which possess emulsifying and detergent properties. This group includes all widely used typical soap and soaplike substances with a hydrocarbon radical of significant length and pronounced polarity of the hydrophilic end.

2 Emulsifiers forming true solution in water. This group includes alcohols, amines and fatty acids.

Emulsifiers of the first group are characterized by

- 1 The ability to lower the surface tension of solution.
- 2 A low value of maximal concentration of dissolved emulsifier.
- 3 At concentrations exceed a critical value, known as critical micelle concentration (CMC), a separation of new phase, called micelle, is formed by the aggregation of emulsifier molecules.

4 The ability of the internal phase of the micelle to dissolve water-insoluble substances, which has been called "solubilization" or "colloidal dissolution".

Functions of emulsifier in emulsion polymerization system are

- 1 Stabilize the monomer droplets in the dispersion medium. The emulsifier molecules are adsorbed on the surface of the monomer droplet with their hydrophilic ends directed towards the dispersion medium. The surface tension between two phases, monomer droplets and dispersion medium, is reduced substantially and the energy required to maintain the individual dispersed monomer droplet is decreased then monomer droplets are stabilized.

2 Emulsifier is essential for formation of polymer particles. Owing to attractive force between their hydrophobic ends, the emulsifier molecules form aggregate, called micelle, when their concentration exist a certain critical value, critical micelle concentration(CMC). A micelle can be visualized as a cluster 50 - 100 emulsifier molecules and $0.005 - 0.01 \mu$ diameter with their hydrophilic ends direct towards the water phase and their hydrophobic ends towards the center of micelle. Since the interior of micelles are strongly hydrophobic, they are able to dissolve certian amount of monomer, this phenomenon is called solubilization. The micelles are much smaller than the monomer droplets, but since their number is usually much larger, their surface area is 1 - 3 orders larger than that of the monomer droplets. When initiators dissociate into primary radicals and enter into micelles, then polymerization begins, thus micelles are the major loci of paticle nucleation.

3 The emulsifiers serve to stabilize the polymer particles being formed during polymerization. During the particles generation period, part of micelle are used for nucleation of polymer particles and part of them disintegrate to deliver emulsifiers necessary for the stabilization of the growing polymer particles. In general, only small fraction of the micelles is used for particle nucleation, most of them desorb to deliver the emulsifiers for particle stabilization.

Emulsifiers increase particle numbers as their concentratin in initial charge is increased. However, stability of particles can be improved by delayed addition of more emulsifier after nucleation is completed without effecting the particle number, particle size or particle size distribution.

The emulsifier are found in three different loci at the begining of reaction. Firstly, dissolve as single molecule in the dispersion medium. Secondly, present as micelle, usually the largest part. Finally, adsorbed on the surface of the monomer droplets. After the polymerization begins, absorbed emulsifiers on polymer particle surface are presented. Without the presence of suitable type and

amount of emulsifier, the polymer particles would coalesce and a stable dispersion would not be obtained.

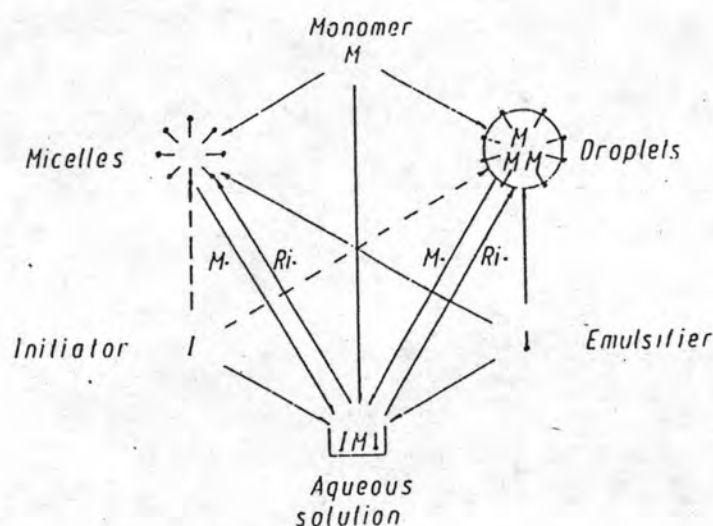


Figure 1.1 Schematic illustration of the components and phases usually present in an emulsion polymerization system. The arrows indicate the possible distribution of components among phases (Priima, 1982).

In the Smith-Ewart theory, Smith and Ewart (1948), as well as in other treatments, Kirillov and Ray (1978), Chiang and Thompson (1979), Kiparissides et al. (1980), Normura et al. (1981), the primary radicals formed by decomposition of initiator in the dispersion medium were assumed to enter micelles and polymer particles. It has been pointed out that these usually ionic, very water-soluble radicals are rarely adsorbed directly into a micelle or polymer particle but must be added some monomer units in the aqueous phase to become sufficiently oil soluble to be absorbed. It now seems to be generally accepted that formation of these oligomers in aqueous phase in the first step in the nucleation and polymerization process. The water-soluble oligomers and primary radicals may be destroyed or nucleate particles. The different possibilities are listed in Table 1.1.

Table 1.1 Reaction possibilities of a radical and an oligomeric radical in the aqueous phase and the probable results.

| Process | Result |
|--|---|
| A Absorption into a micelle | Micellar initiation |
| B Absorption into a monomer droplet | Droplet initiation |
| C Absorption into an earlier formed particle | Radical disappearance (particle growth) |
| D Propagation in aqueous phase | Higher oligomers |
| E Termination in the aqueous phase | Dead oligomers (may or may not be lead to nucleation) |
| F Precipitation in the aqueous phase (self-nucleation) | Homogeneous nucleation |
| G Mixed-micelle formation (with or without emulsifier) | Nucleation (homogeneous or micellar) |

1.2 Advantages and disadvantages of emulsion polymerization

There are many advantages and disadvantages in an emulsion polymerizations system reported in literatures, Hamielec and Friis (1975), Gardon (1977), Eliseeva et al. (1981) and Priima (1982), and are shown below.

1.2.1 Major technical advantages

1 Viscosity of the reaction mixture in emulsion polymerization remains relatively low over the reaction period.

2 Emulsion polymerization has less heat transfer problems, in comparison with bulk polymerization, even at high polymerization rate because water act as a good heat sink medium.

3 No use of expensive solvents in emulsion polymerization system and consequent recovery problems are eliminated, thus the latex polymer can be dried safely without causing fire hazard or air pollution.

4 The using of highly effective emulsifier given in small particles formed in emulsion polymerization. Thus it has a smaller problem in particles coalescence than relative large particle formed in suspension polymerization. So, emulsion polymerization is suitable for the production of sticky, rubbery polymers.

5 Reaction rate and molecular weight from emulsion polymerization process are very high.

6 The ultimate use of final product as latex particle can be made without further separation but require appropriate blending operation.

7 Emulsion polymerization can make large change in molecular weight of polymer from 2×10^4 - 2×10^6 . A large decrease in molecular weight can be made without altering the polymerization rate by using chain transfer agents. Large increase in molecular weight can be made by lowering the initiator concentration or lowering the reaction temperature.

1.2.2 Major technical disadvantages.

1 The production of bulk polymer from emulsion polymerization process must involved coagulation of the latex and drying of polymer. This process requires extra chemicals and equipment.

2 Bulk polymer and latex from emulsion polymerization are contaminated with emulsifiers, pH-buffer, colloid stabilizers etc., which added into the reaction system to avoid catastrophic coagulation of polymer particles. The added materials may have deleterious effects on certain specific properties of polymer such as optical clarity, electrical, mechanical and engineering properties, water absorption, water resistance and adhesion to substrate.

1.3 Emulsion polymerization and suspension polymerization.

Emulsion polymerization and suspension polymerization have many similarities and differences because they are heterogeneous free radical polymerization. The similarities and differences of both processes are shown below, according to Hamielec and Friis(1975) and Priima(1982).

1.3.1 Similarities of the two processes

- 1 Both are homogeneous reactions in the sense that they involve more than one phase in the reaction mixture.
- 2 They are free radical polymerization.
- 3 They have dispersed polymer particles in dispersion medium.

1.3.2 Differences of the two processes

1 The emulsion polymerization initiators are dissolved in aqueous phase while that of suspension polymerization are dissolved in organic phase.

2 The emulsifiers used in both processes are different. Suspension polymerization uses much smaller quantities of emulsifier than emulsion polymerization does.

3 The reaction sites of both systems are completely different. The reaction loci of suspension polymerization are the relatively large monomer droplets that initially present in the system while the reaction loci of emulsion polymerization are the much smaller polymer particles which are generated in situ.

4 Different in final polymer particles. The average particle diameter of emulsion polymerization is of the order $0.1 - 0.3 \mu$ while that of suspension polymerization is $1.0 - 3.0 \mu$ in diameter.

5 Difference in reaction kinetic. The average particle volume of emulsion polymerization is many order smaller than that of suspension polymerization. The difference in particle volume is the major reason for the kinetics of the two processes are different. Emulsion polymerization gives very high rate of polymerization and leads to the

molecular weights which are much higher than that obtained from suspension polymerization.

6 There is no mass transfer between phase in suspension polymerization. The polymerization begins in the monomer droplets in which polymer concentration increase as polymerization proceed, thus the suspension polymerization, polymer particles consist of a solution of polymer in its monomer. Unlike the suspension polymerization, emulsion polymerization reaction occurs in polymer particles, which already in the early stage of reaction and have a relatively high concentration of polymer. In contrast to suspension polymerization, emulsion polymer particle consist of a solution of monomer in its polymer.

1.4 Continuous stirred tank reactor and batch reactor.

The performances of a continuous stirred tank reactor (CSTR) are quite different from that of a batch reactor for a number of reasons, according to Priima(1982).

1 The distribution of reactor residence times in a CSTR is quite broad. This leads to broad size and age distributions of the latex particles. By contrast, the polymer particles in a batch reactor are usually formed near the begining of the reaction and the particle size and age distribution of the latex are narrow.

2 The different behavior in response to inhibitors and/or retarders in the feed streams. In a batch reactor these compounds react near the begining of the cycle and then the polymerization proceeds in a near normal manner. In a CSTR, inhibitors in the feed streams are continuously added to the reactor and serve to reduce the rate of initiation of polymer molecules.

3 Copolymer composition in a batch reactor tends to change with time. The first polymer formed is rich in the more reactive monomer and the final polymer contains more of least reactive monomer. This drift in composition can lead to polymer particles with nonuniform composition in radial dimension. The copolymer from a CSTR

should be relatively uniform in composition if the reactor is operated at steady state. If several CSTRs are connected in series, polymers of several different compositions can be formed.

4 The operation of CSTR involves the addition of the feed streams. Recipe ingredients of CSTR are usually divided into several feed streams. In this case the mixing should be sufficient to blend these streams rapidly with the polymerizing mixture in the reactor. In batch reactor, all ingredients are added near the beginning of the reaction cycle and before the particles are formed.

5 The difference in heat removal. In batch reactor, generated heat can be highly nonuniform. Sometimes the reactor productivity is dependent on the capacity to remove heat during the peak reaction period. Heat removal in CSTR is uniform and higher productivity can be achieved.

6 The reactor fouling. In batch reactor, the batch cycle involves filling and emptying the reactor frequently. A disadvantage of this operation is that the latex can dry and stick to the walls and initiate the formation of wall polymer. The fact that the reactor is emptied frequently provides an opportunity for cleaning. A properly designed continuous reactor system should operate full of latex, without a vapor space. This helps to prevent or retard the formation of wall polymer. In fact the absence of a liquid-vapor interface may show the formation of coagulation in the latex. One disadvantage of a continuous system is that operation in a particular reactor must be stopped for cleaning. If frequent disruptions are required, continuous reactor system will probably not be economically feasible.

7 Difference in molecular weight, branching and crosslinking characteristics. In general, branching, crosslinking and gel effect phenomena become more significant at higher conversions. The final product from a batch reactor consists of molecules formed over a rather broad range of conversion. This is less true in emulsion polymerization than in bulk since the conversion at the reaction site in the polymer particle may be quite high even through the overall react-

ion conversion is low. In a CSTR, the polymer is formed at a constant conversion, that existing under the state of operation. This will be higher than the average conversion over a batch reactor cycle. Thus, branching and crosslinking reactions are normally more pronounced in CSTR systems.