Process Bulletin

Emulsion Polymerization

Description

Emulsion polymerization involves the formation of synthetic latexes and resins by the polymerization of a monomer-in-water emulsion. The resulting polymer dispersion in water may be used in this form, such as for water-based paint, adhesives and the preparation of foam rubber. For other applications the water may be removed by spray drying or other means to produce a free-flowing powder or coagulated cake.

The following materials are frequently polymerized in the emulsion state:

1. synthetic rubber latexes - butadiene-styrene, acrylonitrile-butadiene, polybutadiene, polychloroprene and polyisoprene;

2. coating latex - polyacrylates, polyvinyl acetate, polyvinyl chloride and polyethylene copolymers;

3. plastisol resins (a resin mixed with a plasticizer to make a paste) - polyvinyl chloride;

4. specialty latexes - polyethylene and polytetrafluroethylene.

The ingredients used in an emulsion polymerization are listed in the following generalized recipe (Martens, 1964):

Component	**%-Wet Basis**
Monomers	30 - 50
Surface-active agents	1 - 3
Protective colloid	0 - 3
Initiator	1 - 3
Modifier	0 - 1
Buffer	0 - 1
Water	50 - 70

The initiators of the polymerization are usually water-soluble peroxides, hydroperoxides and persulfates. The emulsifiers may be anionic, cationic or nonionic surfactants. The emulsifiers suspend monomer droplets and polymer particles. Modifiers may be aldehydes, mercaptans or chlorinated hydrocarbons that control the polymerization reaction restricting cross-linking and controlling the molecular weight. Protective colloids, such as polyvinyl alcohol or methyl cellulose, are used to stabilize the final latex. Buffer salts control the pH of the emulsion polymerization batch. These salts, such as phosphates, citrates, acetates and carbonates, are important because pH affects reaction rate, particle size and other reaction conditions.

In some cases the monomer emulsion is seeded with polymer particles. "The purpose of seeded emulsion polymerization is to avoid the uncertainties of the particle initiation stage, obtain better batch-to-batch reproducibility, and give a stable latex of the desired particle size" (Bassett, 1981, p. 199). The reasons for polymerizing in water include: more rapid polymerization than bulk polymerization at the same temperature with a greater average molecular weight; good heat transfer in water with better control of heat of polymerization; all of the monomer is consumed in the polymerization and the resulting latex can be used directly in coating applications; and the aqueous phase lowers the overall viscosity of the emulsion.

Polymerization Mechanism

The monomer emulsion is made up of water-immiscible monomer droplets stabilized by surfactant molecules, empty micelles (colloidal surfactant vesicles) and monomer-swollen micelles. The monomer droplets can range in size from less than one micrometer to ten micrometers. The size of micelles is about 10 to 15 nanometers. During the reaction, the monomer molecules diffuse from the droplet reservoirs to the micelles where polymerization takes place. The polymer chains grow in the micelles. As polymerization proceeds, the monomer droplets decrease in size and eventually disappear. When the polymer particles become large, the surfactant molecules in the micelles suspend the polymer particles. The final polymer particles grow to a size range of a few tenths of a micrometer up to one micrometer. The physical character of the final polymer depends on the temperature of reaction, the formulation and the manipulation of the reaction conditions, such as when and how much of the ingredients are added to the reactor.

Process

The homogenizer is used in emulsion polymerization to emulsify the monomer into the premix to the reactor. Of all the emulsion monomers, vinyl chloride polymerization is the one that most commonly uses homogenizers to prepare the mix.

In a typical process the ingredients to make the polymer are added in the appropriate sequence to an evacuated, agitated, pressurized tank (pressurized with nitrogen gas). After mixing the ingredients and adjusting the temperature of the mix, the emulsion is homogenized to produce the desired monomer droplet size. The homogenizing pressure may be in the range of 1000 to 5000 psi, depending on the monomer and the required droplet size of the monomer reservoir. This monomer droplet size can affect the physical character of the final latex particles. From the homogenizer the emulsion goes to the reactor, where polymerization occurs at a controlled temperature, until the desired conversion is achieved. After completion of the reaction, the latex is cooled and removed from the reactor.

When processing a monomer, such as vinyl chloride, certain safety precautions must be observed. Vinyl chloride monomer is a clear, colorless liquid with a boiling point of -13.3° C (+8 F). It is flammable in air, has a density greater than air and is listed as a known carcinogen. Therefore, special homogenizer design requirements are necessary for processing vinyl chloride monomer.

References

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