LATEX TECHNOLOGY

1. Introduction

Latex technology encompasses colloidal and polymer chemistry in the preparation, processing, and conversion of natural and synthetic latices into useful products.

Latex technology vernacular is not always consistent. By definition a *latex* is a colloidal suspension of polymer particles stabilized by dispersing agents in an aqueous medium. The dispersing agents are conventional ionic or nonionic surfactants or polymeric surfactants made from block or graft copolymers derived from monomers with different hydrophobicities. An *emulsion* (1) is a dispersion of two or more (2) immiscible liquid phases (one being water) stabilized by amphiphilic materials. A latex is a specific type of emulsion; one where the organic phase is a polymer particle. The terms latex and emulsion are often used interchangably partly because emulsion polymerization is the principal synthetic route to latices. Emulsion polymerization is one type of heterophase polymerization involving organic and aqueous phases. Others include suspension, dispersion, and precipitation polymerization which generate water-borne particles different from latices. Heterophase polymerizatio can also involve two immiscible organic phases as in nonaqueous polymer dispersions and polymer microgels. Finally, polymers prepared via homogeneous polymerization, whether in solution or neat, can be inverted into a polymer dispersion in water using surfactants. Similar to latices, these materials can have very different molecular weight and functional group distributions and thus form a separate class of materials.

Latices have been in use for a very long time and the history of latices and polymer development are closely linked. The Mayas (3), around 1600 BC, used the sap of trees like the sparse *Hevea brasiliensis* of South America (4) to make rubber products and waterproof clothing. The Mayas called the sap “caa o-chu,” literally translated as “weeping tree.” *Caoutchouc* is now the French word for rubber. The natural rubber derived from this sap was shown to be 93–95% *cis*-1-4-isoprene by Faraday (5) in the early 19th century. Goodyear's invention of vulcanization, and later the automobile, increased natural rubber demand through the beginning of the 20th century (6). Large rubber plantations in Malaya, Ceylon, Indonesia, and Indochina increased the world's natural rubber production to 200,000 t by 1920. Enhanced supply led to rapid growth of natural rubber products and improvements in latex processing. The Allied blockade of Germany during World War I led to the first process for making synthetic latex (7). Gottlob (8) and others were early developers of emulsion polymerization (at first using methods to duplicate how natural rubber is produced in nature). Soon thereafter, U.S. companies began producing commercial synthetic latices: Buna S (butadiene–styrene copolymer), also known as Government Rubber–Styrene or GR–S rubber; Neoprene (polychloroprene) (9); and Thiokol (polysulfides) (see STYRENE-BUTADIENE RUBBER). Japan's seizure of the Southeast Asia rubber plantations during World War II led to intensive research in synthetic rubber production (10). Today synthetic latex production accounts for 60% of the 18×10^6-t total rubber market (11,12) which has been growing at 2–5% over the last decade. Synthetic latices account for ca 2.5% of the world polymer market

(13,14). Allergic reactions to proteins in natural latex and other natural latex market drivers have recently created more opportunities for synthetic latices (15). Over 70% of the natural latex market is converted to solid polymer for use in tires.

Many synthetic latices exist (16–18). They contain butadiene and styrene copolymers (elastomeric), styrene−butadiene copolymers (resinous), butadiene and acrylonitrile copolymers, butadiene with styrene and acrylonitrile, chloroprene-copolymers, methacrylate and acrylate ester copolymers, vinyl acetate copolymers, vinyl and vinylidene chloride copolymers, ethylene copolymers, fluorinated copolymers, acrylamide copolymers, styrene−acrolein copolymers, and pyrrole and pyrrole copolymers. Many of these latices also have carboxylated versions.

Traditional applications for latices are adhesives, binders for fibers and particulate matter, protective and decorative coatings, dipped goods (especially without allergens), foam, paper coatings including water-proofing paper (19), backings for carpet and upholstery, modifiers for bitumens and concrete, and thread and textile modifiers to improve feel or properties such as flame retardence. More recently latices have found use in biomedical applications as protein immobilizers; as visual detectors in immunoassays, as release agents in drug delivery (20), wound treatment, and synthetic blood (21), in electronic applications as photoresists for circuit boards; in batteries, conductive paint, copy machines; as key components in molecular electronic devices; in specialty coatings for seeds (22), in artificial turf plastics; and as an important component of oil recovery techniques (23). The application of even more specialized latices can be surprisingly complex (24).

2. Latex Properties

The observable properties of a latex, ie, stability, rheology, film properties, interfacial reactivity, and substrate adhesion, are determined by the colloidal and polymeric properties of the latex particles. Important colloidal properties include ionic charge, stability, particle size and morphology distribution, viscosity, solids, and pH. Important polymer properties include molecular weight distribution, monomer sequence distribution, glass-transition temperature, crystallinity, degree of cross-linking, and free monomer. Methods for analyzing each of these properties exist, depending on the end use of the product. Overviews of the various polymer colloid characterization methods are available (25–27) (see also COATINGS).

2.1. Stability. For a latex to be a useful product, control of polymer isolation is crucial. The individual polymer particles must be stable enough to avoid coagulation resulting from perturbances like high temperature, freeze−thaw cycles, high shear in handling, electrolyte addition, and organic solvent addition during processing, but not so stabilized that polymer isolation is impossible. Stability is related to the surface properties of the latex particles, and these are usually determined during latex manufacture (28). Visual detection of coagulation is easy; more sophisticated optical techniques are possible (29). The types of initiator, emulsifier, and monomers used are the key determinants.

Electrostatic Stabilization. The electrical charges on the surface of a latex particle are balanced by an electrical double layer of oppositely and then similarly charged counterions. The outer layer is known as the diffuse electrical double layer, and its potential controls the colloidal stability of the latex particles (30). The diffuse electrical double-layer potential is closely related to the zeta potential. Electrophoresis measurements at various pH and ionic strengths are a means of calculating the zeta potential (31,32). As two particles approach, their individual diffuse double layers begin to overlap and the particles repulse one another. As the particles get even closer, attractive forces build and the particles coagulate. The energy required to overcome the repulsive forces depends on the ionic strength of the bulk phase, the temperature, and the nature of the ions balancing the latex particle charge. Latex particles coagulate at zeta potentials close to zero and are very stable at zeta potentials above 50 mV. One way to coagulate particles is to reduce the energy barrier between particles by adding electrolyte. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (33) is a method for predicting the amount of electrolyte needed to coagulate a latex by first predicting the critical coagulation concentration. DLVO theory does not account for the chemical nature of the electrolyte nor the interaction of the ions with water. Additional mechanisms must often be added to the extended DLVO theory to model more complicated systems (34). Aluminum compounds, such as aluminum alginate, coagulate latices with varying effectiveness depending on the pH of the latex system (35). Protein behavior (36) and even nonaqueous stabilization can be modeled in a similar fashion (37).

Steric Stabilization. Nonionic surfactants, usually containing ethylene oxide units, are able to stabilize particles by adsorbing their hydrocarbon chain ends on the hydrophobic polymer zones of the surface of the latex particle. The ethylene oxide groups extend into the water phase. These compounds suffer from temperature and dilution sensitivity. A–B block copolymers where A is compatible with the latex polymer and B with the dispersion medium offer a more robust method of steric stabilization. Triblock and star block methacrylate copolymers can also act as surfactants providing steric stabilization (38). Reactive macromonomers with affinity toward the dispersion medium copolymerized with hydrophobic monomer offer a chemical way of grafting the stabilizer to the surface of the latex particle (39). Organic solvent addition is used to coagulate sterically stabilized latices (40). Addition of soluble homopolymer can lead to reversible and irreversible flocculation by depletion and bridging flocculations (41).

In general, electrostatic stabilization leads to smaller and more uniform particle size when compared with syntheses involving similar amounts of steric stabilizers. An advantage of non-ionic surfactants over electrostatic stabilization is improved humidity resistance (42). A given class of stabilizer can provide both electrostatic and steric stabilization depending on the length of the steric moieties in the surfactant molecule (43).

Other Stabilizers. In addition to anionic, cationic, and nonionic surfactants used in manufacture of the latex, other specialized surfactants can be added or compounded to the latex after manufacture to increase the stability of the latex. For example, amphoteric surfactants such as *c*-cetyl betaine are used to improve the mechanical stability of low pH anionic compounds. Quaternary ammonium salts are used to improve the mechanical stability of cationic latices and their compounds. They are used either alone or in combination with a nonionic surfactant. Sequestrants (44) such as sodium silicate, sodium polyphosphate, and the sodium salt of ethylene diamine tetraacetic acid are added to anionic latices to retard the destabilizing action of cations that get leached slowly from compounding ingredients containing multivalent ions. The addition of these ingredients is also beneficial if the use of hard water is unavoidable in making and using the anionic latex compound. Care must be taken to avoid shocking the latex during compounding with these additional surfactants.

2.2. Rheology. Flow properties of latices are important during processing and in many latex applications such as dipped goods, paint, inks (qv), and fabric coatings. Rheology is used to characterize the stability of latices (45). For dilute, nonionic latices, the relative latex viscosity is a power–law expansion of the particle volume fraction. The terms in the expansion account for flow around the particles and particle–particle interactions. For ionic latices, electrostatic contributions to the flow around the diffuse double layer and enhanced particle–particle interactions must be considered (46). A relative viscosity relationship for concentrated latices was first presented in 1972 (47). A review of empirical relative viscosity models is available (46). In practice, latex viscosity measurements are carried out with rotational viscometers.

It is possible to increase the viscosity of a latex after manufacture using thickeners. Thickening occurs through increases in medium viscosity or polymer particle aggregation. If considerable aggregation occurs without a corresponding increase in medium viscosity, undesirable separation or creaming occurs. Methylcellulose, caseinates, and polyacrylate salts are typical thickeners. Ease of adding the thickener, ability to maintain viscosity, and undesirable side effects must be considered when selecting a thickener. Some thickeners slowly hydrolyze in the latex and lose their effectiveness over time. The full range of the effects of adding thickener develops over time; some of them are much faster than others. To avoid exceeding the desired viscosity, it is advisable to add thickener in small increments, waiting after each for the viscosity to reach equilibrium before adding the next one.

The viscosity of the latex can also be dependent on pH. In the case of some latices, lowering the pH with a weak acid such as glycine is an effective method for raising the viscosity without destabilizing the system. Latices made with poly(vinyl alcohol) as the primary emulsifier can be thickened by increasing the pH with a strong alkali.

Particle size influences the viscosity of a latex, and the industrial demand for high solids latices has led to bimodal and multimodal particle-size distributions (48). Solids levels approaching 70 wt% are possible. The smaller the particle size, the higher the viscosity.

2.3. Particle Size. The particle-size distribution of a latex is a determinant of its performance in application. Particles are almost always spherical, although nonspherical particles are possible (49,50). Particle-size distributions are now routinely measured using scattering methods, light scattering being the most common and most effective on particles >300 nm. Small-angle neutron scattering (SANS) is useful for concentrated latices and smaller (<ca 300 nm) particle sizes (51). Microscopic techniques are also a reliable method. Two of

the newer techniques are sedimentation field-flow fractionation (52) and capillary hydrodynamic fractionation (53). The particle-size distribution has an impact on stability, rheology, morphology, and film-forming properties. Stability is predicted for larger particles, with broadly distributed particle sizes showing a greater tendency to coagulate owing to interactions between the smaller particles (54). Viscosity effects are weighted to the larger particles. Morphology is affected by particle size, as in the case where the particle size of the polystyrene latex used to seed polystyrene core–poly(ethyl methacrylate) shell particles determined the morphology of the final latex. When the seed was less than 200 nm in diameter, the final particles were prolate spheroids of near-hemispherical polystyrene and poly(ethyl acrylate) domains. When the seed was 300 nm in diameter, spherical polystyrene particles embedded with circular patches of poly(ethyl methacrylate) were the result (55). A review of the fundamental aspects of morpology control has been written by Sundberg and Durant (56).

2.4. Film Properties. Dehydration (57) at temperatures above the polymer glass-transition temperature is the principal means for forming film from latex. Interdiffusion of the polymer chains between particles is thought to be the limiting step in film formation (58). The final properties of the film depend on the polymer in the latex particles. Significant differences can exist between films made from solution polymer and latex polymer, respectively, because of the colloidal debris remaining on the latex polymer (59). Important film properties include hardness, flexibility, clarity, conductance, impact strength, and toughness. Core–shell particles have seen extensive use as rubber-toughening agents.

2.5. Improving Properties Through Compounding. The potential value of most polymers can be realized only after proper compounding. Materials used to enhance polymer properties or reduce polymer cost include antioxidants, cross-linking agents, accelerators, fillers, plasticizers, adhesion promoters, pigments, etc. Antioxidants are essential to retard degradation in unsaturated polymers. Cross-linking agents are used to build modulus, resistance to permanent deformation, and greater solvent resistance in many types of polymers. Accelerators are frequently used to reduce the time and temperature required to affect the cross-linking. Fillers, such as carbon black (qv) and clays (qv), do not reinforce latex polymers as they do their dry polymer counterparts. Rather, they are used in most latex applications to adjust processing rheology and to lower raw material costs of the product, or to impart specific effects, eg, aluminum trihydrate to increase resistance to flame degradation, or carbon black to increase resistance to UV degradation. Plasticizers and oils are used to soften and increase flexibility at lower temperatures, improve resistance to crystallization, or depress the brittle point of the product. Hydrocarbon process oils, glycols, vegetable oils, ester plasticizers, and low melting point resins are some of the common materials used. Many types of resins are added to enhance the tackiness of polymers. Generally, within a class of tackifying resins, the lower the melting point, the greater the tack developed in the compounded polymer. The optimum amount of any resin for maximum tack depends on the type of polymer to which it is added. Resins added as solvent-cut emulsions rather than as solventless emulsion or dispersions develop more tack in the polymer, because the residual solvent in the polymer contributes to the tack of the polymer resin blend. Pigments and dyes are used to impart color. Some pigments with some polymers also impart other effects such as improved water resistance or reduced flammability.

3. Latex Applications

3.1. Adhesives. Latices are used as additives in the construction market, in tires and belt fabrication, in furniture manufacture, in packaging, and in tapes, labels, envelopes, and bookbinding. The adhesives are used in wet or dry laminations. In wet lamination, the adhesive is not dried before assembly; hence at least one of the substrates must be porous to allow for the water to evaporate. Wet lamination has the advantage that the surfaces to be adhered can be repositioned during assembly, provided the solids content remains below the level at which the adhesive begins to form a film. The disadvantage of wet lamination is the slower development of cohesive strength in the adhesive film and the need for closer control of timing when the two substrates are to be brought together; if this occurs too soon, the adhesive film is too weak to hold the assembly together, and if it occurs too late, the adhesive is too dry to effect a satisfactory bond.

3.2. Binders. Latices are used as fiber binders in the paper and textile industries. The two principal methods of application are (*1*) wet-end addition, wherein the ionic latex is added to a fiber slurry and then coagulated in the slurry prior to sheet formation; and (*2*) saturation of the latex into a formed fiber web, wherein the latex is coagulated by dehydration. Latices are also used as binders for particulate matter such as rubber scrap.

3.3. Coatings. Latices are used in residential and industrial paints, coated paper and paperboard, seeds (60), fabric coatings, backing for carpet, upholstery, and drapery; as basecoats for wallpaper and flooring; and in insulation coatings (see COATINGS). Application methods include brushing, squeegee, spraying, dipping, and frothing (see COATING PROCESSES, SURVEY).

3.4. Dipped Goods. Latices are used in various dipping processes to produce balloons, bladders, gloves, extruded thread, and tubing. Manufacturing techniques include multiple dip and dry, and coagulant dipping employing a colloidal destabilizer (61,62).

3.5. Foam Products. Latices are made into foams for use in cushioning applications. The latices are frothed with air and then chemically coagulated for thick applications, or heated to induce coagulation for thinner applications. The latter method allows for infinite pot life during production (see Cellular Materials).

3.6. Modifiers. Latices are added to bitumens, mortars, and concrete to improve impact resistance and reduce stress cracking. Key to the use of latices in these technologies is compatibility between the latex and the construction materials.

4. Synthetic Latex Manufacture

The history of emulsion polymerization has been well documented (63). Early efforts to produce synthetic rubber coupled bulk polymerization with subsequent emulsification (64). The first attempts at emulsion polymerization arose from problems controlling the heat generated during bulk polymerization. In emulsion polymerization, hydrophobic monomers are added to water, emulsified by a surfactant into small particles, and polymerized using a water-soluble initiator. The result is a colloidal suspension of fine particles, 50–1000 nm in diameter, usually comprising 30–50 wt% of the latex product. By 1935 emulsion polymerization became the method of choice in making synthetic rubber because of its many advantages (65): (*1*) the reaction mass viscosity remains low throughout the polymerization, providing for improved heat transfer, agitation, and product handling; (*2*) the sensible heat of the water in the emulsion balances the heat of reaction generated by free-radical polymerization; and (*3*) the rate of reaction is rapid, while producing very high molecular weight.

4.1. Kinetics and Mechanisms.

Early researchers misunderstood the fast reaction rates and high molecular weights of emulsion polymerization (66). In 1945 the first recognized qualitative theory of emulsion polymerization was presented (67). This mechanism for classic emulsion preparation was quantified (68) and the polymerization separated into three stages: nucleation, particle growth while monomer droplets exist, and particle growth once monomer droplets have disappeared.

Stage I: Particle Nucleation. During stage 1 of a typical emulsion polymerization, the reaction mass consists of an aqueous phase containing small amounts of soluble monomer, small spherical micelles, and much larger monomer droplets. The micelles are typically 5–30 nm in diameter and are saturated with monomer emulsified by the surfactant. The monomer droplets are larger, 1000–10,000 nm in diameter, and are also stabilized by the surfactant.

Water-soluble initiator is added to the reaction mass to generate radicals which can enter the very small diameter micelles. Polymerization starts in the mcielle, converting it into a growing polymer particle. As monomer within the particle converts to polymer, it is replenished by diffusion from the monomer droplets. The concentration of monomer in the particle remains high (5–7 *M*), as long as monomer droplets exist. The growing polymer particles require more surfactant to remain stable, supplied from the uninitiated micelles. Stage I is complete once the micelles have disappeared, usually at or before 10% monomer conversion. Typically, 1 in 100 micelles are converted into latex particles, the others sacrificing their surfactant to the larger latex particles.

Primary radicals generated from water-soluble initiator rarely enter a micelle (69) because of differences in surface-charge density. The radicals formed from decomposition of water-soluble initiator are ionic in nature and very soluble in the aqueous phase. The ionic radical water solubility is reduced by polymerization with monomer dissolved in the aqueous phase, a key first step, and the growing ionic oligomer chains become less soluble in the aqueous phase and readily enter the micelles. Radical entry is a thermodynamic balance based on solubility (70). Other theories exist to explain how water-soluble radicals enter micelles (71). The micelles are presumed to be the principal locus of particle nucleation (72) because of the large surface area of micelles relative to the monomer droplets.

However, in the case of miniemulsion, processing methods reduce the size of the monomer droplets closer to the size of the micelle, leading to significant particle nucleation in the monomer droplets (73) and therefore lack of dependence on monomer tranpsort across the aqueous phase. Intense agitation, cosurfactant, and dilution are used to reduce monomer droplet size. Additives such as cetyl alcohol are used to retard the diffusion of monomer from the droplets to the micelles, in order to further promote monomer droplet nucleation (74). The benefits of miniemulsions include inclusion of hydrophobic moieties in latex particles (75), faster reaction rates (76), improved shear stability, and the control of particle-size distributions to produce high solids latices (77). Microemulsion polymerization (78) employs very high surfactant levels to make very small latex particles.

An expression for the number of particles formed during stage I was developed, assuming micellar entry as the formation mechanism (68), where k is a constant varying from 0.37 to 0.53 depending on the relative rates of radical adsorption in micelles and polymer particles, r_i is the rate of radical generation, m is the rate of particle growth, a_{s} is the surface area covered by one surfactant molecule, and S is the total concentration of soap molecules.

$$N_p = k(r_i/m)^{0.4}(a_s S)^{0.6} \tag{1}$$

During stage I, the number of polymer particles range from 10^{13} to 10^{15} per mL. As the particles grow they adsorb more emulsifier and eventually reduce the soap concentration below its critical micelle concentration (CMC). Once below the CMC, the micelles disappear and emulsifier is distributed between the growing polymer particles, monomer droplets, and aqueous phase.

The Smith–Ewart expression (eq. 1) accurately predicts the particle number for hydrophobic monomers such as styrene and butadiene (79), but fails to predict the particle number (80) for more hydrophilic monomers such as methyl methacrylate and vinyl acetate. A new theory based on homogeneous particle nucleation, called the HUFT theory after Hansen, Ugelstad, Fitch, and Tsai, was developed (81) to explain the hydrophilic monomer data yielding more accurate particle number predictions. The HUFT theory has been extended to include precursor and mature latex particle formation (82,83). In homogeneous coagulation theory (82), very small diameter precursors, containing only small amounts of monomer, transform into mature particles through coagulation. Mature particles form only near the end of the nucleation stage and positively skewed particle-size distributions are the result (83).

The debate as to which mechanism, controls particle nucleation continues. There is strong evidence that the HUFT and coagulation theories hold true for the more water-soluble monomers. What remains at issue are the relative rates of micellar entry, homogeneous particle nucleation, and coagulative nucleation when surfactant is present at concentrations above its CMC. It is reasonable to assume that each mechanism plays a role, depending on the nature and conditions of the polymerization (84).

Whatever the nucleation mechanism, the final particle size of the latex is determined during stage I, provided no additional particle nucleation or coalesence occurs in the later stages. Monomer added during stages II and III only serves to increase the size of the existing particles.

Stage II: Growth in Polymer Particles Saturated with Monomer. Stage II begins once most of the micelles have been converted into polymer particles. At constant particle number the rate of polymerization, R_p, as given by Smith–Ewart kinetics is as follows (85):

$$R_p = \frac{10^3 N k_p [M] \bar{n}}{N_A} \tag{2}$$

where k_p is the propagation rate constant, $[M]$ is the concentration of monomer in the particle, N is the concentration of growing polymer particles, n is the average number of radicals per particle, and N_A is Avogadro's number.

During stage II the growing particles maintain a nearly constant monomer concentration. The concentration of monomer is particle-size dependent, with smaller particles having lower concentrations (86).

During stages II and III the average concentration of radicals within the particle determines the rate of polymerization. To solve for $\bar{n}$ the fate of a given radical was balanced across the possible adsorption, desorption, and termination events. Initially, a solution was provided for three physically limiting cases. Subsequently, n was solved for explicitly without limitation using a generating function to solve the Smith–Ewart recursion formula (87). This analysis for the case of very slow rates of radical desorption was improved on (88), and later radical readsorption was accounted for and the Smith–Ewart recursion formula solved via the method of continuous fractions (89). More recently, an algebraic solution (90) to the Smith–Ewart recursion formula was put forth that greatly simplifies the calculation.

The nature of the radical within the latex particle determines its fate; ie, its propensity to desorp, propagate, chain transfer, or terminate. It seems reasonable that an ionic radical will not penetrate deeply into a latex particle but rather anchor its ionic head on the surface or palisade of the latex particle, much the way a surfactant molecule does. Once anchored, the nonpolar tail containing the radical will penetrate into the particle, and reactively diffuse throughout the polymer and monomer solution until either the ionic radical desorbs back into the aqueous phase, the ionic radical terminates with another radical within the particle, or the ionic radical undergoes a chain transfer event with either the monomer, polymer, or a chain-transfer agent within the latex particle. Once a chain transfer event occurs, the new radical becomes nonionic and has a markedly different solublity in the particle and aqueous phases. As the nonionic radical grows in chain length within the particle, it becomes even less soluble in the aqueous phase and becomes less likely to desorb. Such a qualitative description of radical fate was quantified (91) and used to properly calculate the rate of polymerization in a macromonomer-mediated emulsion polymerization of methyl methacrylate.

As the particles grow, they require more soap to remain stable. If soap is not available the particles can destabilize, causing product and process problems.

Stage III: Growth in Polymer Particles with a Decreasing Monomer Concentration. Stage III begins once the monomer droplets disappear. The rate of polymerization decreases with reduced particle monomer concentration.

At high monomer conversion, diffusion control of termination can cause an apparent increase in the rate of polymerization (92). Still further conversion can lead to diffusion control of propagation and a marked reduction in rate of polymerization (93). High free monomer in the final latex can result (94–96) causing product odor and handling problems.

The Smith−Ewart kinetics described assume homogeneous conditions within the particle. An alternative view, where monomer polymerizes only on the surface of the particle, has been put forth (97) and supported (98). The nature of the intraparticle reaction environment remains an important question.

4.2. Basic Components. The principal components in emulsion polymerization are deionized water, monomer, initiator, emulsifier, buffer, and chain-transfer agent. A typical formula consists of 20−60% monomer, 2−10-wt% emulsifier on monomer, 0.1−1.0-wt% initiator on monomer, 0.1−1.0-wt% chain-transfer agent on monomer, various small amounts of buffers and bacteria control agents, and the balance deionized water.

Water. Latices should be made with deionized water or condensate water. The resistivity of the water should be at least $10^5\,\Omega$. Long-term storage of water should be avoided to prevent bacteria growth. If the ionic nature of the water is poor, problems of poor latex stability and failed redox systems can occur. Antifreeze additives are added to the water when polymerization below 0°C is required (99). Low temperature polymerization is used to limit polymer branching, thereby increasing crystallinity.

Monomers. A wide variety of monomers can be used, and they are chosen on the basis of cost and ability to impart specific properties to the final product. Water solubilities of industrially important monomers are shown in Table 1 (100). The solubility of the monomer in water affects the physical chemistry of the polymerization. Functional monomers such as methacrylic and acrylic acid, infinitely soluble in water, are also used. These monomers impart long-term shelf stability to latices by acting as emulsifiers. The polymerization behavior of some monomers, such as methacrylic acid, as well as the final latex properties are influenced by pH. For optimum results with these acids, polymerization is best performed at a pH of ca 2. After polymerization, the latex is neutralized to give adequate shelf stability at tractable viscosities.

When monomers of drastically different solubility (101) or hydrophobicity are used or when staged polymerizations (102,103) are carried out, core−shell morphologies are possible. A wide variety of core−shell latices have found application in paints and impact modifiers, and as carriers for biomolecules. In staged polymerizations, spherical core−shell particles are made when polymer made from the first monomer is more hydrophobic than polymer made from the second monomer (104). When the first polymer made is less hydrophobic than the second, complex morphologies are possible including voids and half-moons (105), although spherical particles still occur (106).

Surfactants. Surfactants perform many functions in emulsion polymerization, including solubilizing hydrophobic monomers, determining the number and size of the latex particles formed, providing latex stability as particles grow, and providing latex stability during post-polymerization processing.

Emulsification is the process by which a hydrophobic monomer, such as styrene, is dispersed into micelles and monomer droplets. A measure of a surfactant's ability to solubilize a monomer is its CMC. Below the CMC the surfactant is dissolved in the aqueous phase and does not serve to solubilize monomer. At and above the CMC the surfactant forms spherical micelles, usually 50–200 soap molecules per micelle. Many properties, such as electrical conductivity, interfacial tension, surface tension, refractive index, and viscosity, show a sudden decrease at the CMC (107). The CMC is temperature- and chain-length-dependent for a given class of surfactants (108). The CMCs of nonionic surfactants are higher than those of ionic surfactants (109).

Surfactants also stabilize the growing polymer particles by overcoming the attractive forces between particles. Anionic and cationic surfactants use electrostatic repulsion forces to negate the attraction. Nonionic surfactants use steric forces to repel the attraction. Figure 1 compares the two stabilizing mechanisms. The ability of a given surfactant to stabilize latex particles is dependent on many factors (110), including surfactant type and concentration, aqueous solubility of the monomer and polymer, agitation and shear rate, temperature, surface tension, ionic strength, and concentration of the monomer and polymer (111).

An a priori method for choosing a surfactant was attempted by several researchers (112) using the hydrophile–lipophile balance or HLB system (113). In the HLB system a surfactant soluble in oil has a value of 1 and a surfactant soluble in water has a value of 20. Optimum HLB values have been reported for latices made from styrene, vinyl acetate, methyl methacrylate, ethyl acrylate, acrylonitrile, and their copolymers and range from 11 to 18. The HLB system has been criticized as being imprecise (114).

Three generations of latices as characterized by the type of surfactant used in manufacture have been defined (115). The first generation includes latices made with conventional (*1*) anionic surfactants such as fatty acid soaps, alkyl carboxylates, alkyl sulfates, and alkyl sulfonates (116); (*2*) nonionic surfactants such as poly(ethylene oxide) or poly(vinyl alcohol) used to improve freeze–thaw and shear stability; and (*3*) cationic surfactants such as amines, nitriles, and other nitrogen bases, rarely used because of incompatibility problems. Portland cement latex modifiers are one example where cationic surfactants are used. Anionic surfactants yield smaller particles than nonionic surfactants (117). Often a combination of anionic surfactants or anionic and nonionic surfactants is used to provide improved stability. The stabilizing ability of anionic fatty acid soaps diminishes at lower pH as the soaps revert to their acids. First-generation latices also suffer from the presence of soap on the polymer particles at the end of the polymerization. Steam and vacuum stripping methods are often used to remove the soap and unreacted monomer from the final product (118,119).

The second generation includes latices made with functional monomers such as methacrylic acid, 2-hydroxyethyl acrylate [818-61-1], acrylamide [79-06-1], 2-dimethylaminoethylmethacrylate [2867-47-2], and sodium *p*-vinyl-benzenesulfonate [98-70-4] that create *in situ* polymeric emulsifier. The initiator decomposition products, such as the sulfate groups arising from persulfate decomposition, can also act as chemically bound surfactants. These surfactants are difficult to remove from the latex particle.

The third generation are latices made with independently prepared surfactant to mimic the *in situ* prepared functional monomer surfactant. These emulsifiers are often A–B block polymers where A is compatible with the polymer and B with the aqueous phase. In this way, surface adsorption of the surfactant is more likely.

Any of these surfactant classes can involve surfactants that react onto the latex particle. These surfactants are known as *surfmers*. If the surfactant also acts as a chain-transfer agent, it is dubbed a *transurf*. Reversible addition fragmentation agents can act as transurfs (120).

Initiators. The initiators most commonly used in emulsion polymerization are water-soluble although partially soluble and oil-soluble initiators have also been used (121). Normally only one initiator type is used for a given polymerization. In some cases a finishing initiator is used (122). At high conversion the concentration of monomer in the aqueous phase is very low, leading to much radical–radical termination. An oil-soluble initiator makes its way more readily into the polymer particles, promoting conversion of monomer to polymer more effectively.

The most common water-soluble initiators are ammonium persulfate, potassium persulfate, and hydrogen peroxide. These can be made to decompose by high temperature or through redox reactions. The latter method offers versatility in choosing the temperature of polymerization with −50 to 70°C possible. A typical redox system combines a persulfate with ferrous ion:

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-} \tag{3}$$

Reducing agents are employed to return the Fe^{3+} to Fe^{2+}. By starting at a lower temperature, the heat of reaction can be balanced by the sensible heat of the water in the emulsion. Temperature profiles from 20 to 70°C are typical for such systems. Care must be taken when working with redox systems to eliminate oxygen from the reactor before beginning the polymerization. The effectiveness of the redox system can be pH-dependent, with the optimum pH range depending on the type of the redox system (123). For higher temperature polymerizations, eg, above 70°C, thermal decomposition of the initiator is used.

A third source of initiator for emulsion polymerization is hydroxyl radicals created by γ-radiation of water. A review of radiation-induced emulsion polymerization detailed efforts to use γ-radiation to produce styrene, acrylonitrile, methyl methacrylate, and other similar polymers (124). The economics of γ-radiation processes are claimed to compare favorably with conventional techniques although worldwide industrial application of γ-radiation processes has yet to occur. Use of γ-radiation has been made for laboratory study because radical generation can be turned on and off quickly and at various rates (125).

The ionic nature of the radicals generated, by whatever technique, can contribute to the stabilization of latex particles. Soapless emulsion polymerizations can be carried out using potassium persulfate as initiator (126). It is often important to control pH with buffers during soapless emulsion polymerization.

Chain-Transfer Agents. The most commonly employed chain-transfer agents in emulsion polymerization are mercaptans, disulfides, carbon tetrabromide, and carbon tetrachloride. They are added to control the molecular weight of a polymer, P_n, by transferring a propagating radical to the chain-transfer agent AX (127):

$$P_{\bar{n}} + \mathrm{AX} \longrightarrow P_n\mathrm{X} + \mathrm{A}\cdot \tag{4}$$

The newly formed short-chain radical A 1 then quickly reacts with a monomer molecule to create a primary radical. If subsequent initiation is not fast, AX is considered an inhibitor. Many have studied the influence of chain-transfer reactions on emulsion polymerization because of the interesting complexities arising from enhanced radical desorption rates from the growing polymer particles (128,129). Chain transfer reactions are not limited to chain transfer agents. Chain transfer to monomer is in many cases the main chain termination event in emulsion polymerization. Chain transfer to polymer leads to branching which can greatly impact final product properties (130).

Other Ingredients. During polymerization and post-processing, the pH of the emulsion is important. Increasing the pH to improve latex stability is achieved usually by adding sodium hydroxide, potassium hydroxide, or ammonia. To avoid causing any localized flocculation because of a rapid increase in electrolyte in a confined area, these ingredients must be added as dilute solutions of around 3% with mild agitation. In some cases, some surfactant may be required to be added along with the dilute alkali. Antimicrobial agents are added for protection against bacteria attack.

4.3. Process. Commercial processes (131) manufacturing latex can be divided into batch, semibatch, and continuous methods. A schematic of typical equipment is shown in Figure 2. The reactor is usually glass-lined, including agitator and thermowell. The remaining tanks are constructed of stainless steel. The reactor is jacketed to allow for heating and cooling between 0 and 100°C. Reactor agitation is chosen to provide adequate mixing while avoiding shear-induced coagulation. The reactor is equipped with a small condenser; reflux is to be avoided to prevent coagulum from forming. A monomer–soap solution is emulsified by a centrifugal pump and fed to the reactor along with initiator, using suitable flow control. Premixing monomer and initiator is to be avoided to prevent premature polymerization in the feed tank. A shot tank is usually required to allow for addition of ingredients in minor amounts.

In the most common production method, the semibatch process, about 10% of the preemulsified monomer is added to the deionized water in the reactor. A shot of initiator is added to the reactor to create the seed. Some manufacturers use master batches of seed to avoid variation in this step. Having set the number of particles in the pot, the remaining monomer and, in some cases, additional initiator are added over time. Typical feed times are 1–4 h. Lengthening the feeds tempers heat generation and provides for uniform comonomer sequence distributions (132). Sometimes skewed monomer feeds are used to offset differences in monomer reactivity ratios. In some cases a second monomer charge is made to produce core–shell latices. In-line instruments can help determine monomer consumption rates and are becoming more frequently employed, especially in the development of new materials (133). At the end of the process, pH adjustments are often made. The product is then pumped to a prefilter tank, filtered, and pumped to a post-filter tank where additional processing can occur. When the feed rate of monomer during semibatch production is very low, the reactor is said to be monomer-starved. Under these conditions, monomer droplets are not present, and intraparticle polymerization takes place under high polymer–low monomer concentrations. These conditions can lead to branched polymer with bi- and trimodal molecular weight distributions (134).

The batch process is similar to the semibatch process, except that most or all of the ingredients are added at the beginning of the reaction. Heat generation during a pure batch process makes reactor temperature control difficult, especially for high solids latices. Seed, usually at 5–10% solids, is routinely made via a batch process to produce a uniform particle-size distribution. Most kinetic studies and models are based on batch processes (135).

Continuous processes have been developed for many of the larger volume synthetic latices (136–140). Most of these processes involve the use of several continuously stirred tank reactors (CSTR) in series. The exponential residence time distribution of a CSTR is broad relative to a batch reactor, leading to broad particle-size distributions. By placing many CSTRs in series, the effective residence time and corresponding particle-size distributions are narrowed. CSTR processes can also suffer from sustained oscillations and multiple steady states, leading to poor reactor and product performance (141). The cause of the oscillations is related to new particle formation. To avoid such oscillations, many processes use a seed latex in the feed stream (142). If premanufacture of seed is not desirable, a tubular reactor can be used to produce seed of uniform particle size (143). Tubular reactors have also been used as loop reactors, where feeds enter and leave a tubular loop in which the circulating flow is much greater than the throughput (144). Cooling water is sprayed directly on the tube to control the reaction temperature. Recently, coagulum has been successfully controlled during tubular production of a latex using pulsatile flow (145).

Foaming represents a persistent problem in the processing and handling of latices. The most effective way to eliminate the presence of foam is to simply avoid its generation. Ways to reduce foam include eliminating the free fall of latex by using dip-pipes, not stirring air into the latex by not agitating with exposed impellers, and not adding dry ingredients laden with adsorbed air directly to the latex. There are many proprietary additives for minimizing generation of foam (antifoaming agents) or eliminating foam (defoaming agents), but there is no one type that works for all latices (see Antifoaming Agents). Only by trial and error can the most effective agent be found for a given compound or process. With any of them, the minimum amount required should be used since their addition tends to cause localized flocculation, poor wetting, lower water resistance, and "fisheyes" in films. Many antifoam agents get absorbed into the polymer or other ingredients in the compound and thus lose their effectiveness over time, particularly if the compound is being recirculated during processing. These conditions necessitate augmentation with additional amounts of antifoaming agent to counter these effects.

Process Modeling. The complexity of emulsion polymerization makes reliable computer models valuable. Many attempts have been made to simulate the emulsion polymerization process for different monomer systems (146–148).

4.4. Other Routes. *High Solids Emulsions.* Latices are made at the highest possible solids content consistent with acceptable viscosity. Latices solids can be increased by centrifuging, creaming, electrodecantation, or evaporation. The latter two techniques, however, are not of commercial importance. Natural rubber latex, 25–40-wt% solids to start, is concentrated to about 60-wt% solids by centrifuging with milk/cream separator equipment. Creaming is commonly used with synthetic polymer latices. Creaming is accelerated by adding solutions such as ammonium alginate and surfactant to the latex. Depending on the initial solids content and type of latex, solids contents of 58–65 wt% are possible.

Soap-starved recipes have been developed that yield 60-wt% solids low viscosity polymer emulsions without concentrating. It is possible to make latices for application as membranes and similar products via emulsion polymerization at even higher solids (149). Solids levels of 70–80 wt% are possible. The paste-like material is made in batch reactors and extruded as product.

Inversion of Nonacqueous Polymers. Many polymers such as polyurethanes, polyesters, polypropylene, Epoxy Resins, and silicones that cannot be made via emulsion polymerization are converted into latices. Such polymers are dissolved in solvent and inverted via emulsification, followed by solvent stripping (150). Solid polymers are milled with long-chain fatty acids and diluted in weak alkali solutions until dispersion occurs (151). Such latices usually have lower polymer concentrations after the solvent has been removed. For commercial uses the latex solids are increased by techniques such as creaming.

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Table 1. **Water Solubilities of Monomers Common to Latex Production**

Monomer	CAS Registry number	Solubility in water at 25°C, mM
n-octyl acrylate	[2499-59-4]	0.34
dimethylstyrene		0.45
vinyltoluene	[25012-15-4]	1.0
n-hexyl acrylate	[2499-95-8]	1.2
styrene	[100-42-5]	3.5
n-butyl acrylate	[141-32-2]	11
chloroprene	[126-99-8]	13
butadiene	[106-99-0]	15
vinylidene chloride	[75-35-4]	66
ethyl acrylate	[140-88-5]	150
methyl methacrylate	[80-62-6]	150
vinyl chloride	[75-01-4]	170
vinyl acetate	[108-05-4]	290
methyl acrylate	[96-33-3]	650
acrylonitrile	[107-13-1]	1600
acrolein	[107-02-8]	3100

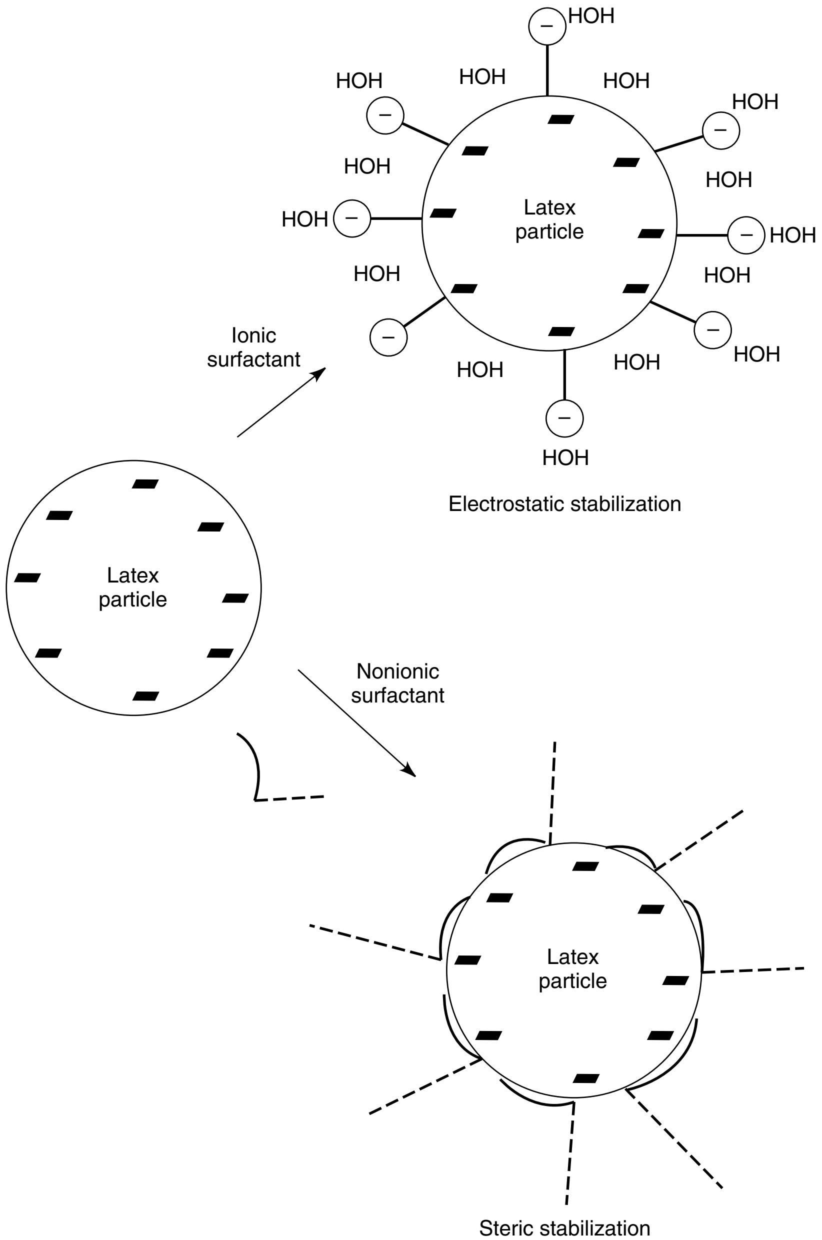

Fig. 1. Surfactant stabilization mechanisms.

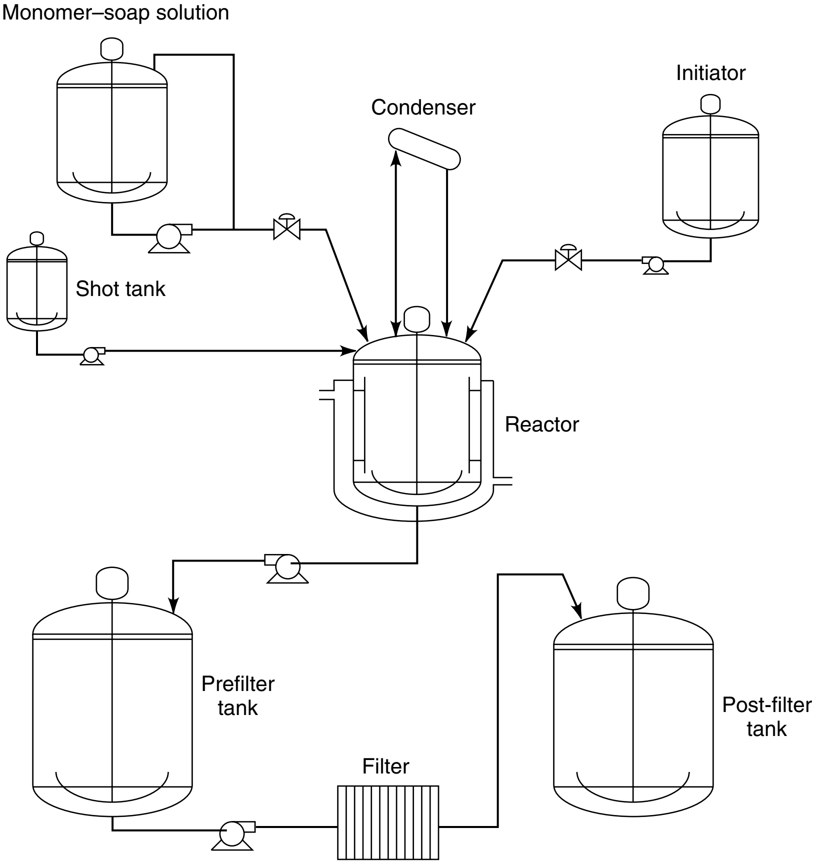

Fig. 2. Typical latex manufacturing equipment.