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Trends in Emulsion Polymerization Processes from an Industrial Perspective

Klaus-Dieter Hungenberg and Ekkehard Jahns

Abstract We highlight some trends in research on emulsion polymerization, focusing on industrial relevance. The review is restricted to a selected (and somewhat arbitrary) number of topics, namely, the use of renewable raw materials, nanostructured latexes, miniemulsion polymerization, continuous emulsion processes, and recent developments in semibatch processes and removal of volatile organic compounds. Scientific and technical details for many of the topics mentioned here are covered by other articles in this volume.

Keywords Continuous polymerization • Emulsion polymerization • Hybrid latices • Miniemulsion polymerization • Multiphase particles • Process control • Renewable resources • VOC removal

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1 Introduction

Emulsion polymerization is one of the most versatile techniques for the production of synthetic polymers, providing materials of varied chemical composition and application. The final product is known as a dispersion, emulsion, or latex, and all terms are used interchangeably in this article.

The semibatch process, in which monomers and other ingredients (initiator, surfactant, etc.) are metered into the reactor, is now the most commonly used industrial process because it offers the unique opportunity to combine chemically different monomers, such as very hydrophobic and hydrophilic monomers, mono- and multifunctional monomers for crosslinked latexes and films, or monomers of low and high glass transition temperatures. Moreover, this process offers the possibility to generate multiphase polymers of various morphologies (see Fig. 1) and to produce composite and hybrid particles that can incorporate other substances such as pigments, fillers, waxes, and active ingredients.

In emulsion polymerization, particle sizes in the nanometer range are inherent to the process itself. No additional operations such as milling or grinding are needed, or high shear equipment, because polymer chain growth occurs through sequential

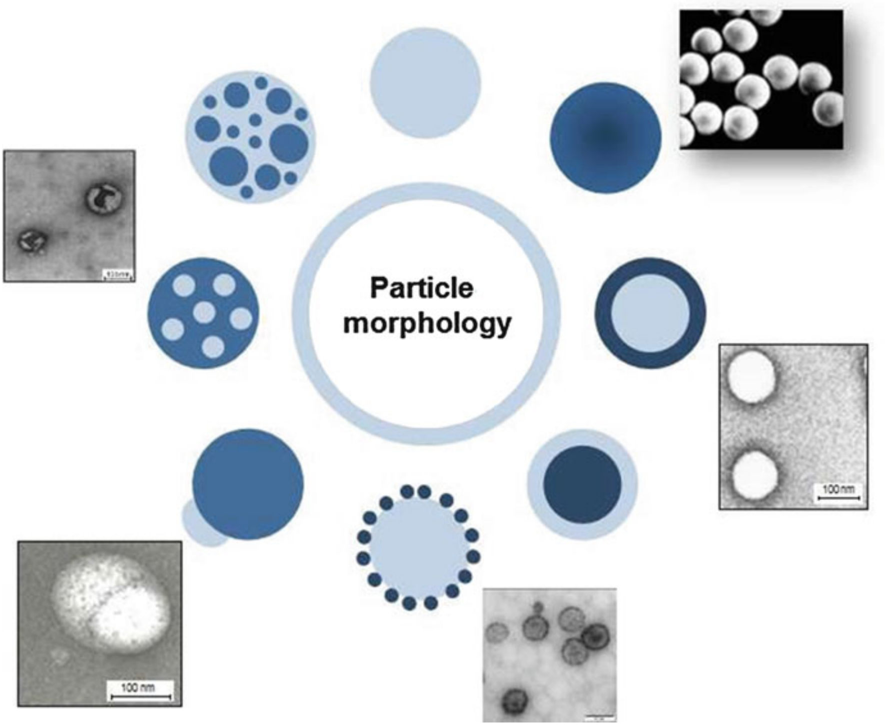

Fig. 1 Examples of possible morphologies of latex particles

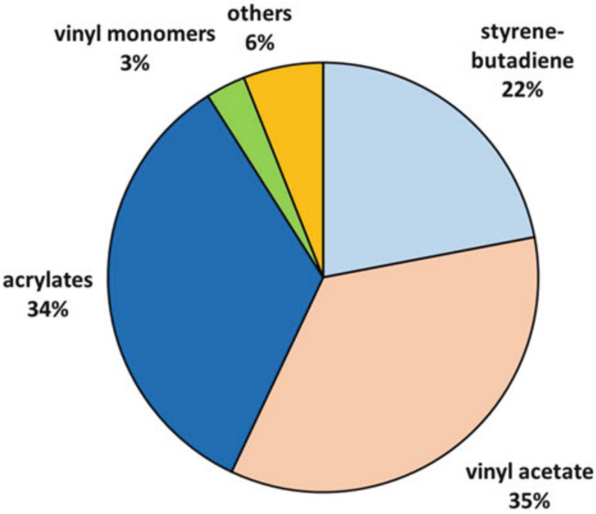

Fig. 2 Estimated market share according to latex polymer class

addition of monomers to latex particles at the nanometer scale. The relatively low viscosity of the system, even for solid contents up to approximately 70% in water, enables the application of simple heat removal technologies. Cooling can be accomplished by conduction through the wall, even for large reactors of up to 100 m^3, but is often complemented by additional (internal or external) heat exchangers or evaporative cooling. This fairly simple technology results in low investment and operational costs and makes emulsion polymerization technology one of the most efficient polymer processes.

Polymer dispersions are often characterized according to the most abundant monomer(s), as shown in Fig. 2. The numbers represent an estimation of market share using data from various sources. Only those emulsion polymers used as a latex are listed, not polymer types that are isolated from the latex (e.g., by coagulation), examples of which are styrene butadiene rubbers for tires and impact modifiers.

In addition to the main monomers, several comonomers are usually included to improve the properties of the latex; examples include water-soluble monomers such as (meth)acrylic acid and (meth)acrylamide derivatives to improve latex stability. Monomers containing epoxy, hydroxyl, or amine groups incorporate reactive moieties capable of undergoing further reactions (e.g., crosslinking) that are useful in the intended application.

Our daily life would be quite different without the use of latexes. They are applied in all kinds of surface coatings as adhesives and sealants, in fiber bonding for paper and textile applications, as foamed latices for cushioning material, and so on. It is not uncommon for the different classes of latexes shown in Fig. 2 to be used in the same application, demonstrating that the application properties of polymer dispersions are largely determined by their colloidal properties and not just by the polymer backbone, as is the case for example in engineering plastics such as polyamides.

The annual production of synthetic polymer dispersions and latexes in 2014 was estimated to be about 21 million metric (wet) tons per year, and the expected high global growth rate of 3–6% per year (depending on region, application, and source) demonstrates the wide applicability of polymer dispersions.

The vendor landscape is as diverse as the chemistry and properties of polymer dispersions; in addition to leading producers such as BASF, DOW Chemical, Synthomer, Celanese, Wacker, and Arkema, there are hundreds of smaller companies with more specialized portfolios. However, this landscape tends to be volatile and is governed by numerous mergers, joint-ventures, and spin-offs.

Drivers for the increasing use of polymer dispersions and for new product development are manifold and depend on the global region. For example, the increased economic and industrial development in countries such as China and India has increased their use of polymer dispersions, especially in paints, coatings, adhesives, paper, and construction products. Regulatory, environmental, and societal issues are important drivers for the switch from solvent-borne to water-borne polymer systems and there is increasing pressure for use of renewable and biodegradable raw materials.

There is an ongoing trend for polymer dispersions to replace polymer technologies that are less environmentally friendly, such as solvent-based polymers and reactive polymers (e.g., epoxy and polyurethane systems) in a variety of applications. Industrial research is still ongoing to broaden and optimize the applicability of polymer dispersions in these applications, mainly as a result of the wide variety of emulsion polymer chemistries and the flexibility of the process (see for example [1, 2]). Blends and hybrid latexes from a wide range of organic and inorganic materials are beginning to enter the market slowly but surely. Polyurethane acrylic hybrids, epoxy acrylic hybrids, alkyd latex hybrids, and nanosilica acrylic hybrids are just a few examples of products of this class. These new materials combine the chemical and application benefits of these chemistries with the flexibility and environmental benefits of emulsion polymers.

2 Renewable Raw Materials

Naturally, there is a trend to replace commonly used monomers derived from fossil feedstock by the same monomers from renewable feedstock [3–5], and there are attempts to introduce new monomers derived from biofeedstock (e.g., linoleic acid [6]). The use of renewable resources involves not only the monomers themselves, but the entire production line. An example is the use of butyl acrylate made from “bio acrylic acid” and “bio butanol” in the production of acrylic emulsions [7].

Moreover, there is a tremendous amount of research into the use of renewable raw materials such as starch and vegetable oils in dispersion formulations [8–11]. However, to date, there has been no real breakthrough because, in many cases, the applications are not yet competitive. Nevertheless, industry is focusing strongly on the use of renewable sources, as shown by the self-defined company strategies of market leaders such as Akzo [12]:

> Our strategic ambitions relating to sustainability performance:
>
> - Increase revenue from downstream eco-premium solutions to 20 percent of our revenues by 2020
> - Reduce our carbon emissions through the value chain by 25 to 30 percent per ton by 2020 (2012 base)
> - Improve resource efficiency across the full value chain

and also from published accomplishments of companies such as BASF [13]:

> To manufacture the binders of the Acronal® brand, the company replaces one hundred percent of the fossil resources used at the beginning of the production process with renewable raw materials.

These are just two examples of the many producers of polymer dispersions that are following similar activities.

It is beyond the scope of this article to review all such developments, but it is worth mentioning that a common problem in the use of feedstock from bioresources is the reproducibility of the feedstock. Irregularities in the feedstock can influence not only reaction rates but also the sensitive colloidal properties during polymerization; On-line measurement and control techniques are applied to detect irregularities in the feedstock as early as possible, and to enable appropriate countermeasures to be taken.

3 Multiphase and/or Composite Particles

Multiphase and/or composite latexes offer the possibility of combining materials with different properties, which are often contradictory or complementary. Reviews on various classes of hybrid latexes have been published recently, for example, by van Herk and Landfester [14] and Asua [15]. Multiphase particles have been synthesized and used for a broad variety of applications that include typical high-volume applications for latexes such as adhesives, coatings with improved barrier or anticorrosion properties, and pigmented coatings; more specialized applications such as tissue engineering, self-healing coatings, and encapsulation of active components for “medium-sized” products; and low-volume, high-value products for gene and drug delivery.

The presence of multiple phases in latex particles may be the result of different factors. If different (co)polymers are synthesized within one particle, they may phase-separate during or after polymerization. The miscibility of different polymers can be estimated from solubility parameters and sophisticated equation-of-state models. Such coexistence of different polymers forming various phases in one particle can also occur in batch copolymerization if the reactivity ratios and/or solubilities of the monomers are very different, resulting in a dramatic shift in the composition of the polymer during polymerization. However, multiphase polymers are usually produced in a more defined way by stepwise semibatch polymerization, whereby various comonomer mixtures are sequentially fed into the reactor. This procedure does not necessarily mean that a core–shell polymer is produced according to the sequence of monomer addition; a wide variety of different morphologies are possible, even for the same monomer system.

The resulting morphology depends on the interplay between polymerization kinetics and the thermodynamics of the system, and is therefore governed by the various physicochemical properties of the system (miscibility of polymers; solubility of monomers in both water and latex particles; degree of polymerization, grafting, and crosslinking; entry and exit rates of radicals into and out of latex particles; glass transition temperature, etc.) and by the polymerization process itself (relative rates of polymerization, "cross-polymerization," mass transport and swelling of the latex particles, temperature, order of monomer feeds, etc.). Several attempts have been made to describe these systems and the resulting families of particle morphologies is shown in Fig. 1 [16–19].

Latexes with heterogeneous morphologies that combine a soft, elastic phase with a hard phase of high glass transition temperature are, for example, used as impact modifiers or in wood coating binders to improve performance. In the latter application, the requirements for low film-forming temperature and high elasticity together with early particle cohesion and good block resistance of the drying coatings are provided by multistage latexes, which generated early acceptance in the market [20]. Hemispheric and multiglobule latex particles are useful as binders to help with contradictory properties such as adhesion versus block resistance (Fig. 3).

Another method employed to generate hybrid systems is to dissolve a polymer (or pre-polymer) in a monomer mixture and then to polymerize the mixture (e.g., via miniemulsion technology [21]). Such hybrid systems may consist of, for example, alkyds, epoxies, polyesters, or polyurethanes. Polyurethanes have attracted enormous attention in the scientific literature in recent years [22]. Polyurethane/acrylic hybrid dispersions, for example, are becoming increasingly important in coating applications. The polyurethane component is acknowledged for its outstanding elasticity whereas the acrylic component enhances outdoor resistance. Not all hybrids are "real" hybrids, which are synthesized together, but are mixtures of separately produced dispersions. The properties of real hybrids can be outstanding, but the high cost of the urethane raw materials is still slowing market acceptance.

A special case in emulsion polymerization is the incorporation of a monomer-induced swelling step in the synthetic scheme. An example of such a scheme is the polymerization of a crosslinked polystyrene latex, followed by swelling of this crosslinked particle with styrene, and polymerization of this second monomer portion to yield "Janus" particles with a hydrophobic surface on one side and a hydrophilic surface on the other side (Fig. 4).

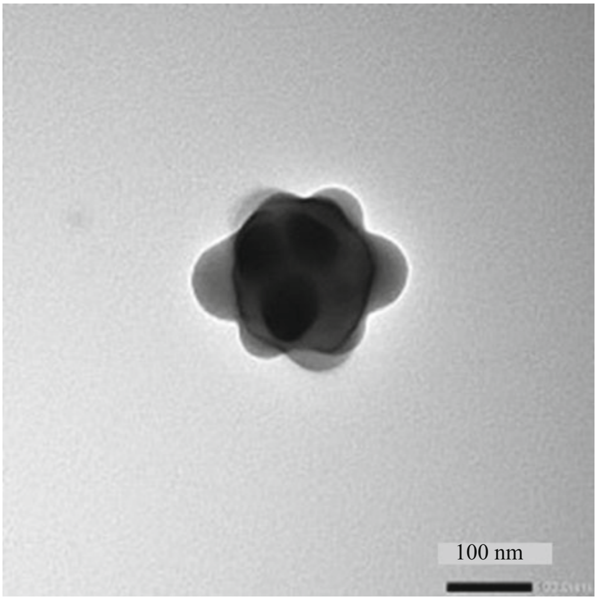

Fig. 3 A 200 nm “raspberry” latex particle (Source: N. Rajabalinia and J.M. Asua, POLYMAT, San Sebastian)

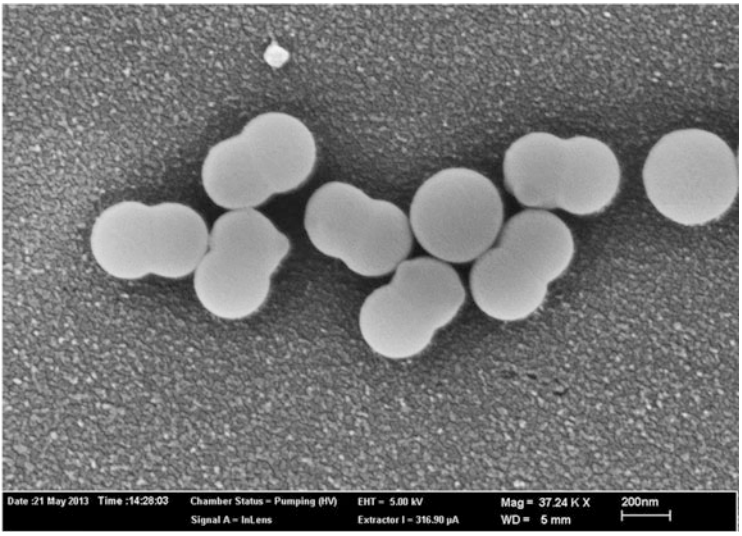

Fig. 4 Janus particles made by swelling emulsion polymerization (BASF SE)

Another type of structured latex particle encloses inorganic material within the latex. These functional materials are manifold and filler materials range from pigments, silicates, magnetic ferrites, and catalysts to, astonishingly, air.

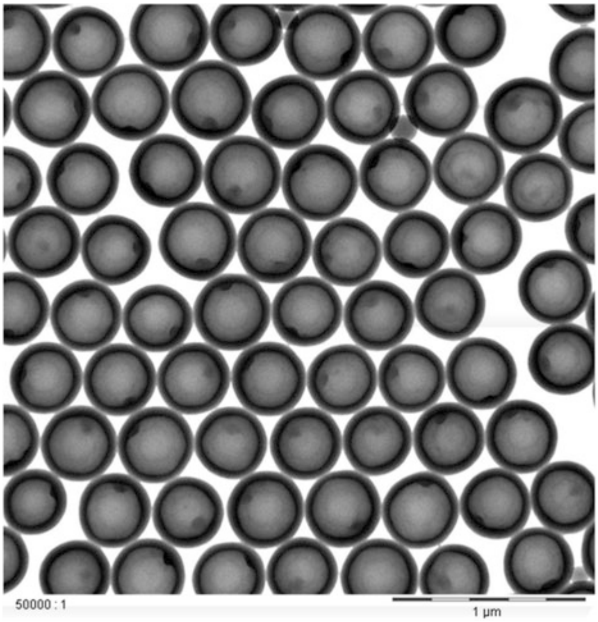

Fig. 5 AQACell® DS6299 from BASF SE

Some of the most sophisticated latex polymer products are used in product lines such as Ropaque® (Dow Chemical) and AQACell® (BASF SE) (see Fig. 5). Hollow spheres are synthesized using an alkali-swellable, acid-rich core, which is then encapsulated by a hard polystyrene shell to yield latex particles with a swollen hydrogel core. The spheres are used in aqueous paint formulations and, as the paint dries, the hydrogel dries out to give an air void without collapse of the shell. The very low refractive index of the air void ($n_D \approx 1.00$) against the high refractive index of the polystyrene shell ($n_D \approx 1.59$) and binder matrix, together with the optimum particle size of about 350 nm, results in high opacity of the formulation by intense light scattering, creating a lightweight "plastic white pigment." This is in contrast to conventional TiO_2 white pigments, which scatter light because of the very high refractive index of TiO_2 ($n_D \approx 2.5$–2.9) against the much lower refractive index of the binder matrix. Combining both technologies, TiO_2 and the "air void" latex together give optimum performance in white paints and coatings.

However, in spite of these possibilities, there are very few commercial applications for multiphase particles on the market (excluding applications for impact-modified thermoplastics, wood coating paints, and clear varnishes). One may ask what the reason is for such a low uptake of this technology, and reach the conclusion that the application advantages do not balance the higher effort required to produce these products. Because the most usual method for their production is via the miniemulsion process, the commercial viability of this process must be improved.

4 Miniemulsion Polymerization

Classical emulsion polymerization is a very versatile polymerization method but there are two drawbacks caused by monomer solubility in water. With highly water-soluble monomers, aqueous-phase polymerization cannot be prevented and, therefore, water-soluble monomers are often polymerized by “inverse emulsion” polymerization, in which water droplets containing the monomer are polymerized in an oil phase. With monomers of low water solubility, the necessary monomer transport from monomer droplets to the locus of polymerization (polymerizing latex particles) is hindered, resulting in a low rate of polymerization. This problem can be overcome in miniemulsion systems by switching the locus of polymerization from the latex particles to the monomer droplets. To achieve this, the monomer droplets must be much smaller (0.05–0.5 μm) than in traditional emulsion polymerization (usually 1–100 μm). Therefore, high shear must be applied to the monomer–water system (e.g., by sonication, rotor-stator equipment, or high pressure homogenizers) in the presence of a suitable combination of surfactant and co-stabilizer. The co-stabilizer is usually a hydrophobic liquid, such as hexadecane, which prevents Ostwald ripening. The small size of the monomer droplets and the resulting high interfacial area has two consequences. First, because of the high surface area, stabilization of the droplet consumes a large portion of surfactant, so less surfactant (ideally none) is left to form micelles, which is (in many cases) where polymerization starts in classical emulsion polymerization. Second, the high surface area of monomer droplets makes them successful in competing with any remaining micelles in scavenging water-borne radicals. Thus, overall, the nucleation mechanism is (ideally completely) switched to droplet nucleation – a mechanism that is usually avoided in classical emulsion polymerization. There are several reviews available on this topic (e.g., Schork et al. [21], van Herk [23], and Asua [15]).

Originally, the advantage of miniemulsions was seen as enabling polymerization of highly hydrophobic monomers in emulsion. This is to some extent still true; for example, the incorporation of long-chain alkyl (meth)acrylates into acrylate formulations can increase their resistance to hydrolysis in acidic environments.

Over time, it has become apparent that the main advantage of miniemulsion polymerization is its ability to produce very complex latex particles, for example, by including various components in the monomer droplets and then polymerizing them, resulting in multiphase/composite particles. However, despite these advantages and widespread research in academia, research institutions, and industry, which has been carried out for more than 40 years since the first publication on this topic [24], the application of miniemulsion polymerization in industry is still rare and limited to some specialty products; examples include UV filters and light stabilizers based on “novel encapsulated additive technology” (NEAT) [25], the Tinuvin® DW family of light stabilizers, and a UV filter for cosmetic application (Tinosorb® S, from BASF SE).

In spite of the importance of miniemulsion polymerization for the synthesis of nanostructured particles and the tremendous interest in this topic in academic research, there are relatively few patents on this subject. There is a striking discrepancy between the scientific and academic interest in miniemulsion polymerization and its commercial importance if one takes the number of scientific publications and the number of patents as the respective measures.

A search for scientific publications on the topic “miniemulsion polymerization,” using Google Scholar for the period 2000–2016, yielded about 16,000 articles (excluding patents and citations). A patent search (ESPACENET of the European Patent Office) on this topic gave approximately 190 results in the worldwide database in the title or abstract; moreover, many of the applicants were from academia. For the same period, there were about 10,000 patents on emulsion polymerization and approximately 85,000 scientific articles.

Thus, for emulsion polymerization the ratio of patent applications to scientific publications was about 1:10, whereas for miniemulsion polymerizations it was 1:100.Even though this is a very rough measure or indication, it does show that real-world applications of miniemulsion polymerization are rare, as are the chances of a breakthrough in the near future.

The reasons have been extensively discussed by Asua [15] and will not be repeated here in detail, but we wish to point out the two main drawbacks that must be overcome before miniemulsion polymerization can become a successful and widespread method for the production of structured nanoparticles.

First, there is lack of knowledge concerning details of the structure required to produce structured nanoparticles, which have superior application properties compared with latexes produced by traditional emulsion polymerization. Important structural aspects are the molecular structure (molar mass distribution, composition distribution, branching, crosslinking, etc.), particle size distribution, and particle morphology in particular.

Second, the miniemulsification step, together with control of droplet size distribution and droplet stabilization throughout the whole process, is crucial for success. A technically and commercially competitive/viable miniemulsification can be summarized as follows:

- Emulsification of 50% or more of an organic phase (eventually containing nanosized particles)
- Viscosity ranging from 1 mPa·s for pure monomer systems to around 10^3 mPa·s for systems with preformed polymer
- Droplet size of 200–500 nm
- Narrow droplet size distribution
- Time scale that does not extend typical cycle times for emulsion polymerization
- Production of several tons per hour

There is no generally applicable method available that fulfils all these requirements. Relatively cheap solutions such as static mixers (with low investment and maintenance costs) generally need hundreds of passes to obtain the required droplet size. Sonication is, in principle, an excellent method because the cavitation effect generates shear within the liquid, but it is difficult to achieve droplet sizes below 1 μm and the technique is generally limited to small quantities. More sophisticated and expensive devices are rotor-stator and high-pressure homogenization systems, which, in spite of the additional high investment, do not generally give satisfactory results. Consequently, existing applications are usually restricted to some special applications that fulfil some of the criteria listed above.

From a mechanistic aspect, it is a challenging task to ensure that nucleation occurs in the monomer droplet and does not arise from homogeneous or micellar nucleation. Generally, this must be considered on a case-by-case basis in terms of chemistry and mode of reactor operation.

In summary, although miniemulsion polymerization is an established and specialized form of emulsion polymerization, there is still a lot of work to do with respect to fundamental understanding of structure–property relationships in order to design superior properties for a range of applications. Furthermore, developments in chemical engineering are needed to overcome process challenges.

5 Semibatch Emulsion Polymerization

The semibatch approach is the most widely used process for emulsion polymerization of different grades because it offers the highest flexibility and allows control of the polymerization process, rate of polymerization (and, thus, rate of heat production), and properties of the latex, such as composition, particle size distribution, molecular weight distribution, gel content, and morphology.

According to the way monomer is fed to the reaction, one can distinguish between monomer feed and emulsion monomer feed (also known as pre-emulsion feed). Monomer feed requires a minimum of equipment because there is no need for any emulsification apparatus. Because all of the surfactant is charged at the beginning of the process, particle sizes are usually small and thus prone to coagulation. If transport of monomer into the latex particles is not fast enough, droplet nucleation can occur, resulting in unwanted coarse material. Moreover, the rate of polymerization is often limited by the rate of transport of monomer to the latex particles.

Monomer pre-emulsion feed requires an emulsification device, which in most cases is a stirred tank, but static or dynamic mixers are also used (see, for example, Kostansek [26]). The amount of emulsifier in the reactor changes throughout the reaction and must be carefully balanced to allow sufficient surface coverage of latex particles and monomer droplets to guarantee stabilization but should not exceed the critical micelle concentration (CMC) in order to avoid secondary nucleation.

However, in some cases, secondary nucleation is a desired phenomenon and is used to produce latexes with a bimodal size distribution to increase the solid content of the dispersion. A second generation of particles can be initiated by addition of “seed” particles, or by addition of surfactant to rapidly exceed the CMC and start a second generation by micellar nucleation [27–29].

With respect to the relative rates of polymerization (rP) and monomer feed (rF), one can distinguish between two extreme cases: monomer-flooded, with rP $<$ rF, and monomer-starved, with rP $>$ rF. Although the first mode offers the opportunity to run at the highest polymerization rate as it operates at the highest monomer concentration in the latex particles, it is seldom used. Disadvantages include the formation of polymerized monomer droplets, increased risk of runaway reactions, poor control of copolymer composition, poor particle size control, and reactor fouling.

Using monomer-starved conditions, the process is mass-transport controlled and thus more easily accessible to reaction engineering measures and control actions. The rate of polymerization, and hence the rate of heat production, can easily be controlled by the monomer inlet mass flow, as is also the case for copolymer composition (identical to the feed composition under starved conditions). Semibatch polymerization is the method of choice for the production of structured particles, such as core–shell particles, by emulsion polymerization.

The disadvantage, however, is obvious – the process runs with a lower polymerization rate than would be possible from the kinetic point of view. Moreover, the rate of heat production must always be kept lower than the heat removal capacity of the reactor. In most cases, recipes for emulsion polymerization are developed for constant monomer feed rates and, generally, constant reaction temperature (without taking into account disturbances during processing of an individual batch, and variations from batch to batch). Disturbances include an increase in fill level, increase in viscosity, variation in feed temperature, varying levels of impurities, and fouling of the reactor wall. The operation of a large-scale reactor with such a fixed recipe must be rather conservative to capture all these variations.

Safety measures must be taken to safeguard the reactor against unforeseen disturbances (e.g., failure of pump, cooling water, or stirrer systems). In addition to conventional mechanical devices such as rupture discs or safety valves, an on-line safety concept [30, 31] can be applied, which limits the amount of unreacted monomer in the reactor by monitoring conversion using on-line calorimetry and by quantitatively updating the actual hazard potential in terms of runaway temperature and pressure. If a potential violation is observed, feeds to the reactor are interrupted or slowed.

There are also examples of emulsion and inverse emulsion polymerization that do not involve heat removal and the polymerization is performed in an inherently safe adiabatic and very fast process [32, 33]. A minimum of safety measures are necessary, but overall controllability is poor.

On-line conversion information, obtained by on-line calorimetry or other methods (see for example Frauendorfer et al. [34] and Fonseca et al. [35]), is a valuable source of information on the state of the process and a prerequisite for improving the performance of a reactor.

Figure 6 gives an example of process variations during one batch emulsion polymerization and between different batches of the same product in terms of the cooling temperature required to keep the reactor temperature at the desired value. During the first half of the reaction, the available cooling capacity is not fully exploited; in principle, one could feed monomer faster and lower the cooling temperature appropriately. Moreover, different batches behave differently, for example because of different states of fouling or different feed temperatures, and some could be run faster than others.

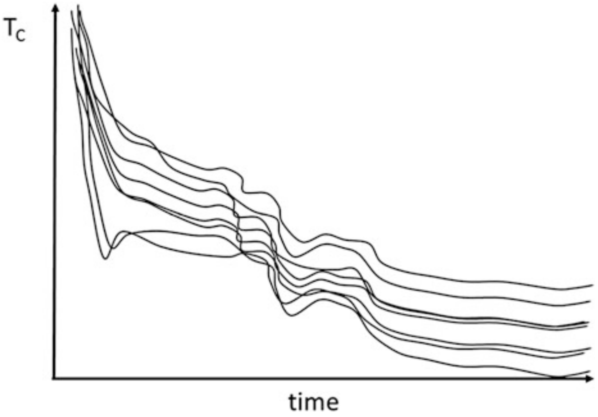

Fig. 6 Cooling water temperature during the course of an emulsion polymerization with fixed feed rates and constant reactor temperature for various repeat batches

To optimize the yield in such a situation, simultaneous control of monomer feed rates and cooling water temperature is necessary. Pelz et al. [36] describe a control scheme for time-optimal operation of a semibatch emulsion polymerization reactor, taking into account jacket temperature constraints and avoidance of a monomer droplet phase. Vicente et al. [37] experimentally verified the on-line control of composition and molar mass during emulsion polymerization in a laboratory-scale reactor. More examples of the application of nonlinear model predictive control (NMPC) to the optimization of (semi)batch processes can also be found in Bonvin et al. [38] and the abovementioned publications.

Despite the highly sophisticated academic research and the promising results in this field, very little has been reported on the industrial application of NMPC for polymer processes in general, and emulsion polymerization in particular. Finkler et al. [39] describe an application for minimization of batch duration in an industrial reactor for solution polymerization, and Graichen et al. [40] report implementation of feedforward control for a polymerization process.

There could be several reasons why NMPC control schemes in (semi)batch polymer processes in industry are not being implemented, and some improvements and changes are required to foster their application. The cost and effort needed for model development, implementation, and maintenance is currently high compared with the benefit, although a 10% reduction in batch time has been reported [36]. Acceptance by plant personnel is important, because the controller actions of an NMPC system might be quite different to those of a conventional proportional-integral-derivative (PID) controller to which the operators are accustomed. The conventional time-controlled recipe (i.e., carrying out the same operation at the same time for every batch) is often part of the quality concept. This concept is violated by NMPC control actions. For example, instead of constant monomer feed rates over a predetermined time interval for every batch of a certain grade, the monomer feed rate is (more or less steadily) changed according to the actual state of the batch (see Fig. 6). Time-optimal NMPC implementations often neglect the properties of the polymer as end-point constraints (e.g., molar mass averages or distributions, composition, branching, or particle size) or, if they do, it is usually done in an open-loop way based on more or less exact models (e.g., Vicente et al. [37] and Gomes [41]), which are prone to uncertainties. Moreover, taking polymer properties as sole end-point constraints is usually not sufficient. Depending on the controller actions, concentrations are prone to changes throughout the process and the accumulated polymer properties may differ accordingly; therefore, the polymer properties should also be set as path constraints in many cases. Moreover, reliable, fast analytical on-line methods for monitoring polymer properties to close the control loop are rare, especially for emulsion polymers where the polymer properties are hidden in the latex particle. There is a strong need for further development of on-line sensors (hard or soft) for monitoring polymer properties and, thus, opening the way to closed control loops.

The overall productivity of the reactor and product quality are determined not only by the efficiency of heat removal from an emulsion polymerization reactor, but also by factors (e.g., homogeneity of the reactor content, coagulum formation) that depend on the fluid dynamic behavior of the reacting mixture. Coupling of population balances with computational fluid dynamics tools [42] to describe the evolution of particle size distribution and, simultaneously, mixing behavior is a valuable method for scale-up and optimization of reactor geometry (stirrer, baffles) and operation conditions such as stirrer speed or position of feeds and their composition.

6 Continuous Emulsion Polymerization

There are several continuous emulsion polymerization processes in use, especially for large-scale products such as rubbers [43] and polyvinylchloride, but also for copolymers from vinyl acetate and ethylene (e.g., de Castro and Adams [44], and Hain et al. [45]). In most cases, a series of continuous stirred tank reactors (CSTRs) are used, or combinations of CSTR and tubular reactors. Sometimes, the CSTR is mimicked by a loop tubular reactor [46]. Continuous emulsion processes in reactors with the residence time distribution of a CSTR have to face a serious problem, namely the occurrence of damped or sustained oscillations, which result in multiple steady states for conversion and variations in the properties of the latex and polymer (e.g., particle size or molecular weight and their distributions) [47]. A method of choice to avoid such oscillations is to shift the nucleation process outside the CSTR, either by using a seed latex in the feed or by placing a tubular reactor before the CSTR [48].

In recent years there has been a strong trend to process intensification for polymer production by replacing the conventional and flexible (semi)batch reactors by continuous reactors. Durand and Engell [49] describe the incentives for such a switchover: “In continuous production, on the other hand, the heat removal capacity is larger so that higher reaction rates (solids contents) can be realized, and hence the space-time yield is higher. Moreover, continuous processes can be more tightly controlled and require less cleaning as long as there are no product changeovers. The switch from batch to continuous production is one facet of process intensification which can lead to savings of energy and material, more compact and thus cheaper plants and improved sustainability and better economic performance." A large European research project, "Flexible, Fast, and Future Production Processes (F3 Factory)," led by the European chemical and pharmaceutical companies Bayer, BASF, Arkema, AstraZeneca, Rhodia (now Solvay), and Evonik has been instigated that targets the development of continuous standardized plants of small to medium scale .

Over the years, several promising results on the transfer from batch to continuous processes have been published. The group of Moritz reported continuous emulsion polymerization in reactors with superimposed secondary flow [50]. Rossow et al. [51] describe an example of a tubular reactor. An overview on recent developments in this field is given by Asua [52], together with examples of the transfer from semibatch reactors to a cascade of CSTRs. Other examples relate to the use of sieve-plate columns as a tubular reactor [53].

However, despite these and other successful examples at the laboratory scale, a real breakthrough has not yet been achieved and there are still several economic and technical questions, as well as problems, that need to be resolved.

The fact that polymers, especially emulsion latexes, are products by process is usually mentioned but the consequences are often underestimated. Polymer structure, colloidal properties, and application-related properties are different for different processes. Many latexes are produced as a range of specialized grades, and so an entire product portfolio has to be developed for a new process. Moreover, new research infrastructure, at both laboratory and pilot scales, has to be established for a new process. It must be carefully analyzed whether the product(s) under consideration for a switch to continuous process manufacture are suitable for such a transition in terms of product volume, number of necessary grade changes, stockholding, and many other aspects.

The widespread argument that the use of continuous reactors leads to lower operational and capital costs is not always true and must be carefully considered in each case. The same holds true for the argument that continuous processes yield less out of specification (off-spec) material than semibatch reactors. The use of modern control and automation tools also makes the generation of off-spec material a rare event in batch processes.

There are also a number of technical problems to be resolved, which are more or less problematic depending on the reactor set-up and its residence time distribution and geometry. Problems such as fouling, plugging, and cleaning of the reactor are of operational relevance, whereas conversion, solid content, performance of grade changes, and residual monomer are of economic relevance. The achievable polymer structure (molar mass, composition, branching, crosslinking, and their distributions) and colloidal properties are issues related to product quality.

The problems and questions discussed above for the change from a semibatch to continuous process seem to be especially challenging for emulsion polymerization, with its multiple phases, compared with solution or bulk processes.

7 Removal of Volatile Organic Compounds

Regulatory and societal requirements for reduced VOCs in paints, coatings, etc. makes the post-treatment of latexes an important process step. Despite its importance, there are only a few scientific articles on this topic. Araujo et al. [54] review monomer reduction in polymer systems in general. There are, in principle, two ways to reduce VOCs – chemical and physical. Chemical measures usually comprise post-polymerization in the reaction vessel itself or in a separate vessel by adding a fast-reacting initiator system comprising peroxides and reducing agents (so-called redox systems). Ilundain et al. [55] present an experimental and theoretical investigation on the post-polymerization of vinyl acetate dispersions.

At first glance, chemical VOC removal seems to be the method of choice because it can be carried out easily, without any extra investment, in the polymerization reactor itself. Alternatively, removal can take place in a post-reactor, which can be of a much simpler and cheaper design than the polymerization reactor itself because it operates at ambient pressure and without heat removal. However, post-polymerization can only reduce the concentration of polymerizable monomers; the concentration of other VOCs (e.g., saturated analogues of the monomers) remains unchanged. Furthermore, low molecular weight oligomers/polymers resulting from the high flux of radicals during chemical VOC removal may change the properties of the latex. Radicals from the post-polymerization initiator system might not (or to a limited extent) enter the latex particles, so only water-soluble monomers are significantly reduced and hydrophobic monomers remain mostly unaffected. Decomposition products from organic peroxides and/or reducing agents contribute to the overall VOCs. As the initiator system reacts rapidly, even before being homogeneously distributed in the reactor, locally increased levels of electrolytes or increased pH values can cause coagulum formation. This inhomogeneity increases the use of the initiator well above the theoretical requirement.

Consequently, in many cases, physical measures are used alone, or together with post-polymerization techniques to reduce VOCs in polymer dispersions. Kechagia et al. [56] present a study on the combination of both methods. Stripping of aqueous dispersions, usually with the aid of steam, air, or nitrogen, is the most frequently used physical method. Different types of apparatus can be employed and vessels [57], columns [58], and thin-layer evaporators [59] have been described (see also Englund [60]). Using this technology, nonpolymerizable VOCs can also be removed, but this process step requires additional investment and still has an obvious drawback – reduction of high-boiling compounds is limited because of their high boiling points and poor water solubility. Thus, it is difficult to remove compounds such as long alkyl chain (meth)acrylic esters, or 4-phenyl cyclohexene and 4-vinyl cyclohexene, which are Diels–Alder reaction products from styrene and butadiene (in styrene–butadiene dispersions).

In addition to steam and air, supercritical carbon dioxide has been used as processing aid in the devolatilization of latexes [61, 62]. However, the study was limited to the removal of monomers such as styrene and methyl methacrylate, and did not investigate the removal of high-boiling components.

8 Summary

Even though the emulsion polymerization process is over 100 years old, there is still a lack of detailed knowledge and understanding of the process, which makes it a challenge from both the scientific and industrial points of view. The transfer from scientific insights and findings in academia to an industrially viable application is not straightforward and usually takes time and the serendipitous occurrence of suitable opportunities. Such opportunities may come from customer demands, legislative regulations, societal requests, raw material issues, market pressure, and many more. Last, but not least, the implementation of new technologies must have an economic benefit for industry.

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