Modelling an Emulsion Polymerization Process by a Population Balance Equation with Competitive Growth Rates

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Abstract

This contribution describes a model of the dynamic evolution of the particle size distribution (PSD) in a seeded emulsion polymerization in which the latex particles have different growth rates. The model makes use of the Population Balance Equation (PBE) as a tool for modelling of the PSD. The growth rate, which is the core of PBE, and its impact on the velocity and the shape of the PSD is described. Finally, the validation of the model is demonstrated using experimental data for the emulsion polymerization of styrene taken from the literature. A reasonable agreement between simulated and experimental data was observed albeit some imperfections was observed. The results support the correctness of the submodels of the mechanisms occurring in the emulsion polymerization model.

1 Introduction

An important property of many particulate processes is the PSD that affects the end-use properties of the product. In emulsion polymerization the PSD determines the rheological properties, the maximum solid content, the film forming, drying time, etc. Mayer et al. [1] address the effect of the PSD on the viscosity, and hence the advantage of a bimodal distribution. Rawlings and Ray [2] found that the rate of polymerization and the molecular weight of the polymer produced depend strongly on the particle size and thus it is expected to be influenced by the shape of the PSD. The production of a high solid content latex demands the control of the PSD. Therefore, the modelling of the PSD does not only serve for the design of control trajectory purposes but also for the modelling and improvement of the other features and mechanisms in emulsion polymerization.

The objective of this paper is to study the evolution of the PSD over time and the dependency of the particle growth rate on the size of the particles.

2 Model development

Population Balance Equation (PBE): The PBE considers a distribution of entities (ψ) distributed through a region V of a geometric space (xyz) and through a region R of property

space embedded in an environment with dynamic states X (the physical properties change). It is supposed that the entities are countable and that their number is large enough such that one can consider the population density as a continuous function. Consequently, $\psi dV dR$ represents the total number of entities finding themselves simultaneously in the region x to $x + dx$, y to $y + dy$, z to $z + dz$, ξ_1 to $\xi_1 + d\xi_1$,..., ξ_m to $\xi_m + d\xi_m$. Under these circumstances the PBE reads:

$$\frac{\partial \psi}{\partial t} + \sum_{i=1}^{3} \frac{\partial \{v_i(x,t)\psi(X,\xi,t)\}}{\partial x_i} + \sum_{j=1}^{m} \frac{\partial \{G_j(x,X,\xi)\psi(X,\xi,t\}}{\partial \xi} = h(x,X,\xi) \quad (1)$$

in which $\psi(x,\xi,t)$ is the population density function, $v_i(x,t)$ and $G_j(x,X,\xi)$ are field velocities in spatial and property directions, respectively.

The function $h(x,X,\xi)$ will have different forms in different processes. This term covers phenomena like the formation of new particles by nucleation or the agglomerative merging of two particles into a single particle and conversely. More details about the derivation of a PBE and its relation to the classical *Lioville* equation can be found in [3].

Process description: In a conventional emulsion polymerization, an aqueous dispersion of monomer(s) is converted by free-radical polymerization into a stable emulsion of polymer particles of $0.1 - 1$ μm in diameter. A typical emulsion polymerization recipe comprises the dispersing medium (water), monomer(s), a water soluble initiator and a surfactant (e.g. sodium or potassium salts of saturated long-chain acids). The emulsifier serves as a stabilizer for polymer particles and monomer droplets and its excess forms micelles (ca. 5-10 nm in diameter). A very small part of the monomer can be found in the solution, some is solubilized by the micelles but most stays in the monomer droplets (ca. 10 μm in diameter). The polymerization occurs either in the interior of the micelles (micellar nucleation) or in the continuous phase (homogenous nucleation). The latter occurs when the monomer is at least slightly soluble in the aqueous phase.

PBE in emulsion polymerization We consider the following assumptions in order to simplify equation (1) applicable for emulsion polymerization:

- The reactor is a batch system with respect to particles (no inflow or outflow of particles).

- The reactor is well-stirred so we may accordingly dispense with the spatial coordinates.

- The solids content of the reactor is low enough such that coagulation of particles is negligible.

With the above assumptions and taking the volume of a particle as the property coordinate, equation (1) is converted to:

$$\frac{\partial \psi(V,t)}{dt} + \frac{\partial(G(V,X)\psi(V,t))}{\partial V} = 0 \quad (2)$$

with the following boundary and initial conditions:

$$\begin{cases} \text{B.C.:} & \psi(V_{crt}, t) = R_{nuc} \\ \text{I.C.:} & \psi(V, 0) = \psi_0 \end{cases}$$

where V_{crt} is the minimum volume in which nucleation occurs and R_{nuc} is the nucleation rate. Equation (2) is called a "pure growth PBE". It is evident that the growth rate in this equation is the governing term and it will be analyzed in the next section.

Growth rate kernel: A definition for the particle growth which describes the reaction rate in a single particle is required. The accuracy of the particle growth equation is of prime importance because it specifies the velocity and the deformation of the field ψ. A widely accepted particle growth relation is given by [2]:

$$G(V) = \frac{k_p MW_m M(V) \bar{n}}{\rho_p N_A} \tag{3}$$

where $G(V)$ is the growth rate of a single particle, ρ_p is the density of polymer, MW_m is the molecular weight of monomer, k_p is the propagation rate coefficient, $M(V)$ is the concentration of monomer inside a particle and $\bar{n}$ is the average number of radicals in a particle. $M(V)$ and $\bar{n}$ are the dynamic states in the model established by the mass balances. It is assumed that the values of ρ_p and k_p are constant which is a plausible assumption in isothermal conditions. The manipulation of the growth rate can easily be performed in a semibatch scenario by changing the rate of monomer and initiator addition.

Monomer distribution: Monomer diffuses into the particles in an extremely fast rate as has been reported in [2], [5]. The equilibrium solubility of monomer in the polymer particles is weakly affected by the molecular weight of the polymer or the amount of emulsifier on the surface of particles, but it appeared to be strongly dependent on the size of the particles. Morton's equation was extended in [2], wherein the concentration of monomer can be obtained from the following relationship:

$$\frac{2\gamma}{r} \frac{MW_m}{\rho_m R_g T} + (1 - \phi) + ln(\phi) + \Psi(1 - \phi)^2 = ln(\frac{M_w}{M_{sat}}) \tag{4}$$

in which γ is the interfacial tension between the particle and the aqueous phase, r is the particle radius, MW_m is the monomer molecular weight, R_g is the universal gas constant, T is the reactor temperature, Ψ is the Florry- Huggins interaction parameter, M_w is the aqueous phase monomer concentration and M_{sat} is the aqueous phase monomer concentration at saturation and ϕ is the monomer volume fraction in a particle. Typical results as shown in Figure 1, indicate that smaller particles have significantly lower monomer concentrations what results in a competitive growth rate of particles and consequently a broadening of the PSD.

Average number of radicals per particle: In order to calculate the average number of radicals per particle, $\bar{n}$, the approach of Li & Brooks [4] was implemented. This method
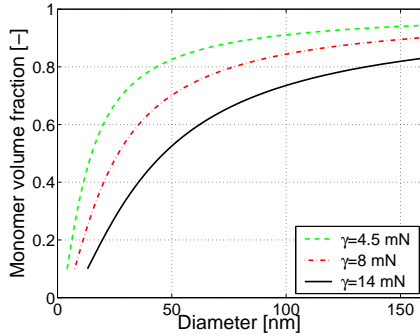
Figure 1: Morton's approach results

Ingredient	Amount (g)
Seed	75.0
Styrene (feed)	24.0
Surfactant	1.0
Initiator ($K_2S_2O_8$)	1.0
Buffer: ($NaHCO_3$)	1.0
Distilled water	480.0
Feeding time	140.0 (min)

Table 1: Recipe used for the semibatch polymerization of Styrene at $50°C$

produces an expression for predicting changes in $\bar{n}$ that gives accurate results over a wide range of conditions. It takes the form:

$$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - f(k_t/\nu)\bar{n}^2 \tag{5}$$

in which σ is the average rate of radical entry into a single particle, k is the rate coefficient for radical exit from the particle, k_t is the rate constant for termination and ν is the volume of the particle. The average volume of particles is used to model this variable.

Additional concerns: The model contains the monomer and initiator mass balances, equations for the free-radical concentration in the aqueous phase, equations of entry and exit of radicals into and from particles. The distribution of monomer between aqueous and polymer phase was calculated using partition coefficients. More details about the model can be found in [6].

The numerical solution of a PBE usually requires the discretization of the particle volume domain into a number of discrete elements. That results in a set of nonlinear differential or algebraic/differential equations that is to be solved numerically. Here, the PBE was transferred to a set of ODE's by implementing orthogonal collocation on finite elements with Lagrange polynomials as basis functions and two internal collocation points for each finite element. The full model was run in the MATLAB® environment using the ode15s solver.

3   Model Results Analysis

In order to validate the results of the model and to determine the computational performance, the semibatch operation of a styrene emulsion polymerization was studied. This monomer has no significant solubility in water, thus the particle formation in the aqueous phase is negligible. Starved conditions where the monomer feed rate is lower than the monomer consumption rate (by polymerization) were considered [5]. It is known that the shape of the

PSD for the initial stage of the emulsion polymerization is sensitive to the nucleation modelling assumptions as well as to the mechanisms of particle formation. In order to alleviate this dilemma, both model and experiments start from a seed distribution. The recipe taken from [5]is given in Table 1. In the following graphs the vertical axes show the weight of the particles thus the integral of each curve always gives the total weight of polymer in the reactor. Figure 2(a-c) show the PSD 25, 50 and 110 minutes after the commencement of polymerization. The behavior of the distributions obtained experimentally and from simulation are in qualitative accord albeit there are some discrepancies especially at the end of the reaction. Despite this good agreement, the broadening effect (competitive growth) ob-
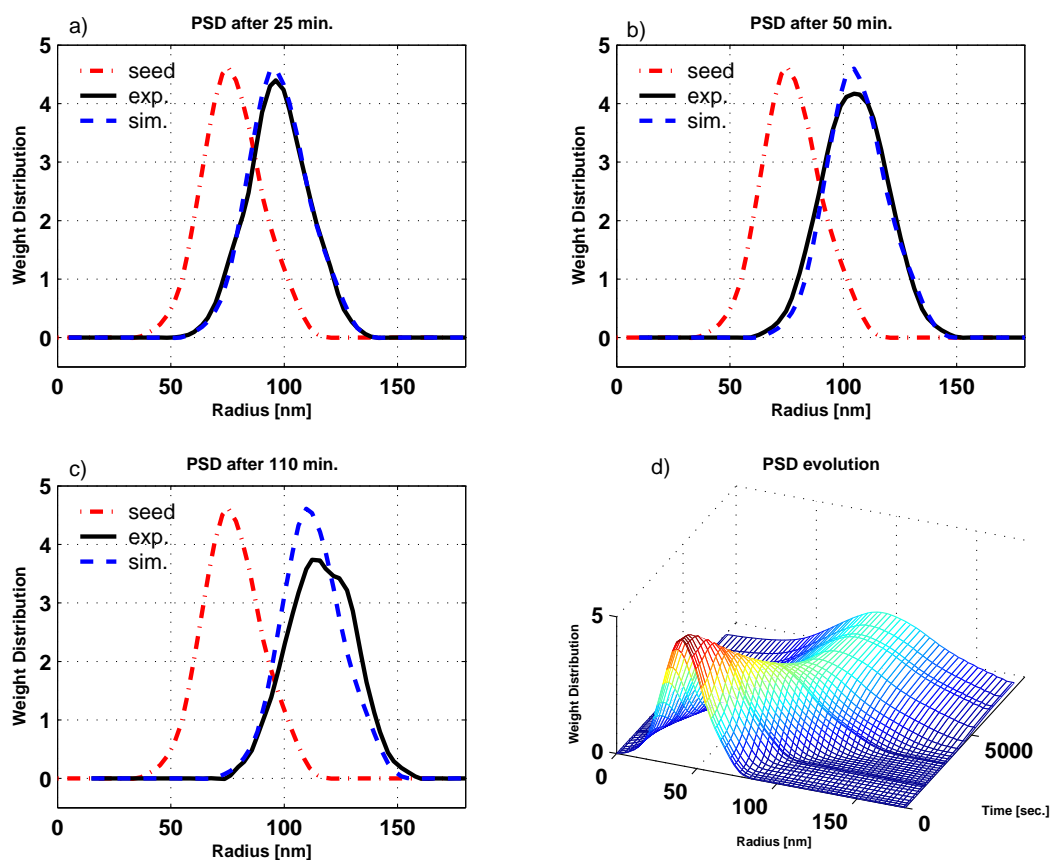

Figure 2: Simulation Results in Comparison with Experimental Data

served in the experiments is not completely predicted by the model. Firstly, Figure 1 shows that the rate of change of the monomer volume fraction for large particles is not alone sufficient to induce a significant deformation of the PSD. Secondly, the sensitivity analysis of the uncertainty of the interfacial tension (γ) in Morton's equation, Figure 1, shows that this parameter does not change the profile too considerably, particularly for large particles. Therefore a model modification (in other words a growth rate modification) is necessary.

Referring to equation (5), $\bar{n}$ is another parameter which does alter the shape and change the velocity of the distribution. This equation is a function of the particle volume, and in the current work, the average volume of particles was used to calculate $\bar{n}$. The modification of $\bar{n}$ is possible by using the approach of Li & Brooks for each cluster of particles separately. A first implementation shows that this modification has a strong effect on the broadening of PSD, Figure 2(d). Finally, the experimental distribution in Figure 2(c) shows a negative skewness at the diameter of 120 nm which maybe due to the difference in the growth rate of the particles in this cluster in comparison to other clusters or coalescence of particles inside this cluster or inaccuracies of the measurements. The latter explanation is the most reasonable one because the former ones are global phenomena and do not occur for a particular cluster.

4   Conclusions and Future Work

It has been shown that a population balance equation with a competitive growth rate is able to predict the evolution of particle size distribution (PSD) in emulsion polymerization suitably. Morton's equation predicts that the broadening of the PSD for small particles is significant while being of less importance for larger particles. It is suggested that a consolidation of Morton's approach and a distributed form of the equation of Li & Brooks, equation (5), can improve the simulation results for the evolution of the PSD further.

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