Particle Size and Particle Size Distribution of Emulsion Polymers: A Review of Modeling Studies

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Abstract: The aim of this work is to provide a literature review in the area of modeling of particle size and particle size distribution of emulsion polymers. Modeling studies of emulsion polymerization are of great interest due to the industrial importance of latexes produced. There are two broad strategies adopted to model particle size distribution: 1) Lumped model in which average particle size assuming the monodispersed distribution is modelled. 2) Distributed model or population balance model in which full particle size distribution is modelled. Lumped model serves as a learning model and a stepping stone to develop a population balance model.

Key Words: Emulsion polymerization, Lumped model, Population balance model, Particle size distribution, Review.

1. INTRODUCTION

Particle size and particle size distribution (PSD) are essential parameters affecting several end use properties e. g. rheological behavior, maximum solid content, ability to form films, etc. of the latex products. Models of PSD of latexes are desirable for producing high-quality products and designing efficient industrial processes and optimizing the classical processes. Model-based approaches are ideally placed to support and accelerate such activities. However, for this to happen in practice, models need to progress as well. In particular, their predictive character must increase considerably and, the time required for their development must decrease [1].

2. EMULSION POLYMERIZATION

Emulsion polymerization was first used on an industrial scale during World War II to produce synthetic rubber. It is now chosen to produce millions of tonnes of synthetic polymer latexes, which include most synthetic elastomers and water-borne coatings, and a significant part of plastics. Around` 13.3 million tons of emulsion polymers (dry basis) were utilized in 2016. Their market value was $36.4 billion, which has risen at the rate of 6.9% per year from 2016 to 2020. At this rate, the market is forecasted to cross $47.5 billion in 2020, showing a nearly 30.6% increase in 4 years. This is environmentally governed in order to remove volatile organic compounds [2]. An overview discussing the fundamentals of emulsion polymerization, which is a rapidly developing industry making a foray into a newer area like the biomedical field, has appeared recently [3].

2.1. Recipe Components

Typical recipe components are dispersion medium, monomer, initiator, and emulsifier. In general, the dispersion medium is water. A simple recipe consists of water (40-60 parts by volume), monomer (40-60 parts by volume), and small amounts of initiator and emulsifier. Generally, industrial recipes are much more complex than the afore-mentioned recipe. Monomers polymerized by way of the emulsion polymerization process include styrene, butadiene, isoprene, chloroprene, methyl acrylate, butyl acrylate, vinyl chloride, vinyl acetate, acrylonitrile, acrylamide, ethylene, and many others.

2.2. Phase and Location of Components

A number of distinct phases exist in a reactor. One or more of these phases may or may not be present depending on the mode of reactor operation or reaction interval. Physio-chemical phenomena occurring within these phases and at the interfaces affect the kinetics of polymerization. These distinct phases, viz. aqueous phase, micelles, monomer droplets and the polymer particles, play important roles during polymerization. Radicals are produced in the aqueous phase. Monomer droplets provide monomer to growing polymer particles. Polymer particles are the sites for free radical’s entry, propagation, exit, and termination. Micelles are the sites for micellar nucleation.

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2.3. Reaction Kinetics

Emulsion polymerization follows free radical addition polymerization, superimposed on a multiphase, compartmentalized system [4]. Free radical addition polymerization consists of four reactions: (i) initiation, where a radical formed by initiator decomposition reacts with a monomer molecule to form a monomer radical. Not all radicals formed by initiator decomposition begin polymer chains and are lost as unreactive products; (ii) propagation, where the monomer radical reacts with monomer molecules to form a long polymer radical; (iii) transfer, in which a growing polymer radical abstracts a hydrogen or halogen atom from another compound to terminate the polymer radical and form a new radical; (iv) termination in which growing polymer radicals combine to give a polymer molecule or disproportionate to give two polymer molecules.

With water-soluble initiators, the initiation reaction occurs only in the aqueous phase, while the remaining three reactions take place predominantly in the particle phase. The formation of the particle phase, commonly known as nucleation, is an important stage which must be considered in emulsion polymerization. The particles receive radicals from the aqueous phase.

3. MECHANISTIC FRAMEWORK

The development of particle size distribution with time is governed by three phenomena: particle nucleation, particle growth and particle coalescence. These are considered together using the population balance approach.

3.1. Population Balance

A dispersed phase system contains two phases: a continuous phase and a dispersed phase. The dispersed phase contains a population of particles. These particles can be differentiated from one another by a number of distinct characteristics which may be grouped into the following two coordinates: the internal coordinates and the external coordinates. Particles with the same internal coordinates may show a different behavior, depending on their position which is defined by the external coordinates, in a non-uniform continuous phase. The framework to describe how particles alter their characteristics is called the population balance [5]. In a well-mixed emulsion polymerization reactor, differences due to external coordinates will not occur and one needs to account for internal coordinates only. The latex particles may be differentiated as per their size, number of radicals, chain length of these radicals; the choice is governed by what governs the analysis. If particles are differentiated according to their size, the number concentration (F(v,t)dv) of the particles is given by:

$$\frac{\partial[F(v,t)V_R]}{\partial t}+\frac{\partial[R_vF(v,t)V_R]}{\partial v}=\frac{1}{2}\int_{v_m}^{v-v_m}k_cF\big(v-v^{"},t\big)F(v^{"},t)V_Rdu-F(v,t)\int_{V_M}^{\infty}k_cF(v^{'},t)V_Rdu,\ldots\ldots v>v_m \tag{1}$$

Boundary Condition

$$\frac{\partial[F(v_m,t)V_R]}{\partial t}=R_n,v=v_m \tag{1.1}$$

Initial Condition

$$F(v,0)V_R=\{Fv_s,0)V_Rifv=v_s0\ldots\ldots\ldots\ldots=otherwise \tag{1.2}$$

The first term on the left-hand side of the equation (1) gives the time variation of the particle density function F(v,t). The second term gives the change of F(v,t) with respect to particle volume (v) due to the growth of the particle by polymerization. The first term on the right-hand side of equation (1) gives the formation of particles in the size range (v, v+dv) due to the coalescence of two particles of volumes v-v' and v'. The factor 1/2 compensates for the two times counting of particle pairs present in the integration. The last term of equation (1) gives the removal of particles in the size range (v, v+dv) due to coalescence of particles of size v with other sized particles. The boundary condition gives the rate at which particles are nucleated at the size (vm), which defines the smallest particle size. The initial condition represents two cases: (i) when seed particles are there in the reactor and then the density function corresponds to that of the seed particles, (ii) when no particles are present in the reactor at the initial time.

The above equation relates the particle growth rate (Rv), nucleation rate (Rn) and coalescence rate. kc is the coagulation rate constant. These phenomena are discussed in the following sections.

3.2. Particle Growth

Particles change their sizes due to the polymerization reaction. The particle growth rate of particles (Rv) is represented by (2), which gives the polymer mass growth rate (in gm (polymer)/sec):

$$R_v=\frac{dm_p}{dt}=\frac{k_pi\varphi d_M}{N_a} \tag{2}$$

Equation (2) contains two variables: ī and Φ. Their calculation is discussed below.

3.2.1. Monomer Volume Fraction in the Particle (Φ)

$$\frac{2\gamma MW_M}{r\rho_M R_G T} + [1\text{-}\Phi + \ln\Phi \text{-} \chi(1\text{-}\Phi)^2] = \ln(\frac{[M]_W}{[M]_{sat}}) \quad (3)$$

Due to the fast rate of monomer transport into the polymer particles [6-7], one can assume that Φ is given by equilibrium considerations. Φ is calculated from the relationship (3) [8-10].

3.2.2. Average Number of Radicals Per Particle ($\bar{\imath}$)

Models for emulsion polymerization are based on the 0-1 kinetics or pseudo-bulk kinetics. These two approaches are discussed elsewhere [11-13]. Small particles, low initiator concentrations, and a large number of particles favor the 0–1 kinetics, whereas the large particles, high initiator concentrations, and a small number of particles will favor pseudo-bulk kinetics.

$\bar{\imath}$ is given by equation (4), which is the recursion relation given by Smith and Ewart [14]:

$$k_e[F_{i\text{-}1}(v,t)\text{-}F_i(v,t)] + k_{des}[(i+1)F_{i+1}(v,t)\text{-}iF_i(v,t)] + \frac{k_t}{2vN_a}[(i+2)(i+1)F_{i+2}(v,t)\text{-}i(i\text{-}1)F_i(v,t)] = 0 \quad (4)$$

The solution of this equation given by Stockmayerand O’Toole [15, 16] for the average number of radicals per particle which is applicable to pseudo-bulk kinetics is:

$$\bar{\imath}(v,t) = \sum_{i=0}^{\infty}\frac{iF_i}{F(v,t)} = \frac{a}{4}\frac{I_b(a)}{I_{b\text{-}1}(a)} \quad (5)$$

Here I_b (a) is the modified Bessel function of the first kind of order b and argument a, and

$$a = 4(\frac{\nu N_a k_e}{k_t})^{\frac{1}{2}} \quad (5.1)$$

and $b = \frac{2\nu N_a k_{des}}{k_t}$ (5.2)

Here, a is the ratio of the radical entry rate constant to radical termination rate constant inside the particle and b is the ratio of radical exit rate constant to radical termination rate constant inside the particle.

Alternate approaches to 0-1 and pseudo-bulk approach are the 0-1-2 [17] or 0-1-2-3 [18] approaches as used by some authors recently. Recently, Ordonez [19] has also calculated $\bar{\imath}$ by including the nucleation and coagulation rates.

3.3. Particle Nucleation

The generation of particles that are polymerization loci is known as nucleation. There are four nucleation phenomena that may occur simultaneously in emulsion polymerization. These are micellar nucleation, homogeneous nucleation, coagulative nucleation and nucleation in monomer droplets. Review of nucleation mechanisms in emulsion polymerization was given by Sood [20]

3.4. Particle Coalescence

Particle coalescence is a mechanism, which if present in the reactor, will influence the latex particle size distribution. Coalescence refers to the phenomena in which the association between the two particles results in such close contact between them that, with subsequent thermal diffusion, they merge together to form another particle [21]. Normally, it is also referred to as coagulation. During emulsion polymerization, coagulation can be caused by insufficient particle stability or by polymerization of monomer in a mode other than normal emulsion polymerization [22]. There are three basic mechanisms explaining particle aggregation due to insufficient stability: Brownian coagulation (perikinetic coagulation), shear coagulation (orthokinetic coagulation) and surface coagulation. Poor dispersion due to insufficient agitation can create monomer pools for bulk polymerization. This different polymerization mode can lead to coagulum formation.Fora recent review on experimental and modeling studies on particle coagulation, one is referred to the work of Cheng *et al.* [1].

4. LITERATURE REVIEW

Excellent review on modeling of emulsion polymerization has appeared in the literature in the recent past but the scope of this review was limited to phenomena associated with particle size distribution viz. the progress made in developing the population balance models and the solution of the resulting modeling equations [23]. In this review, some modeling works are discussed in adequate detail starting from the classical work of Min and Ray [8].

Min and Ray [8] reviewed the models of emulsion polymerization up to 1974. They established a general modeling framework which allowed more detailed predictions. Their general framework permitted a lot of quantitative description than had been attainable before.

Min and Ray [9] in their second paper discussed a computational method based on the method of moments for the elaborate solution of a batch emulsion polymerizationmodel for methyl methacrylate. The model predictions matched experimental data reasonably well.

Cauley *et al.* [24] solved a population balance model of continuous emulsion polymerization analytically. The model was simplified by assuming 0-1 kinetics. The desorption mechanism was incorporated in their model. The model predicted the particle size distributions.

Kirillov and Ray [25] established a mathematical model which was validated against the literature data on continuous methyl methacrylate polymerization reactors. It was applicable to both steady-state and dynamic conditions. Multiple steady states and sustained oscillations for some operating conditions were predicted by the model.

Kao *et. al.* [26] developed a model to describe the conversion versus time profiles of the seeded styrene emulsion polymerization. Both the collision and diffusion mechanisms were considered for radical capture. The collision mechanism gave a good match with the experiment. The model predicted that the rate of polymerization was dependent on the latex particle diameter to the 2.5 power in the gel region, as shown experimentally by Vanderhoff *et al.* [27].

The work of Penlidis *et al.* [28] was a review of works in batch, semi-continuous and continuous latex reactors. Advances made in the areas of gel effect, molecular weight development, particle nucleation, and the dynamics of continuous emulsion polymerization were reviewed. The inclusion of the detailed chemistry and physics of polymerization phenomena in the comprehensive reactor models gave the design of improved systems.

Dougherty [29] developed the SCOPE dynamic process model for batch and semi-batch emulsion co-polymerization. The model included the mass balances for the reacting species and energy balances for both the reactor and the cooling water jacket. Model predictions were validated for styrene-methyl methacrylate co-polymerization under different experimental conditions in Part II [30].

Rawlings and Ray [31] developed models for CSTRs. The models predicted the steady-state multiplicity and dynamic stability structures. The predictions were validated for methyl methacrylate polymerization. The residence time and radical exit rate were important variables influencing reactor stability.

Rawlings and Ray [32] developed a class of simplified emulsion polymerization model.The model was solved analytically using contraction mapping. It was shown that radical exit and certain types of impurities strongly influenced the reactor stability.

Rawlings and Ray [33] developed a detailed population balance model for the prediction of batch and CSTRs. The population balance equations were solved by orthogonal collocation on finite elements. The model’s reliability was shown by a few comparisons with experimental data. A parametric sensitivity study was conducted.

Rawlings and Ray [34] developed a comprehensive model for emulsion polymerizationand model predictions were compared with polymerization of styrene, methyl methacrylate and vinyl acetate in continuous reactors. Acceptable agreement between model predictions and experimental data was found with a single set of parameters. The model predicted several phenomena like steady-state multiplicity, sustained oscillations, ignition and extinction dynamics, and overshoot during start-up.

Rawlings developed simplified emulsion polymerization models for the distribution of particle sizes and radical numbers which were solved analytically [35]. The model was validated for CSTR data. The model predicted sustained oscillations and multiple steady states.

Tauer and Muller [36] formulated a mathematical model for the continuous emulsion polymerization of vinyl acetate. It was used to investigate whether or not sustained oscillations of latex properties occur at high conversions. A good qualitative agreement was found with the experimental data.

Paquet and Ray [37] developed a model for emulsion polymerization in a tubular reactor containing an axial dispersion coefficient to fit measured residence time distributions and to model axial mixing. Acceptable agreement between model and experimental data was found.

Mayer *et al.* [38] developed a detailed steady-state model for the continuous production of seed latexes in a pulsed pack column. The model included micellar nucleation and plug flow with axial dispersion. The model predicted well the experimental data for styrene.

Kiparissides *et al.* [39] developed a comprehensive and simplified model for the emulsion polymerization of vinyl acetate in a CSTR operating under conditions of sustained oscillations. The comprehensive model solved for the age distributions of polymer particles and the simplified model assumed discrete nucleation periods.

A mathematical model was developed by Ordonez and Olayo [40], which included micellar and homogenous nucleation, particle formation by both initiator-derived and desorbed radicals and thermodynamic considerations. In a subsequent paper, Ordonez and Olayo[41] compared their model developed against experimental data of styrene. The model results agreed with the experimental data of conversion and the polymerization rate.

Immanuel *et al.* [42] formulated a mathematical model for PSD in a vinyl acetate-butyl acrylate co-polymerization which employed the pseudo-homo-polymerization approach. Orthogonal collocation on finite elements was used to solve the population balance equations and DASSL was used to solve differential-algebraic equations. The predictions were matched with experimental datafor a semi-batch reactor.

Sood [43] developed a population balance model which was employed to define conditions that will favor the production of monodisperse latexes. It was concluded that the lower emulsifier amounts, higher initiator amounts and higher reaction temperature favor narrower distributions and in some cases monodisperse distributions for the emulsion polymerization of styrene.

An efficient solution method was given by Immanuel *et al.* [44] for population balance models accounting for nucleation, growth and coagulation (with extensions for breakage).

Sood [45] studied through a model the influences of several variables which included the initial initiator amount, the initial emulsifier amount, the monomer addition mode: batch or semi-batch, and the monomer addition rate under “monomer-starved conditions” for the control of PSD.

Coen *et al.* [13] developed a model to calculate conversion and number of particles formed for systems which followed pseudo-bulk kinetics during particle formation and applied it to butyl acrylate emulsion polymerization. The model predicted the experimental data with acceptable accuracy.

Fortuny *et al.* [46] developed a population model to account for both micellar and homogenous nucleation, as well as particle stabilization and growth.

Arora *et al.* [47] proposed a model with the inclusion of vaporization from the liquid phases in the reactor to the gaseous phase. Modeling results showed that a significant amount of heat could be removed by evaporative cooling thus, leading to higher productivity.

Sajjadi [18] proposed a population balance model for the PSD in the monomer-starved semi-batch emulsion polymerization of styrene with a neat monomer feed. Modeling results showed that at the completion of nucleation the particle size is reduced and the PSD narrows with decreasing rate of monomer addition despite nucleation time increasing.

Sood [20] developed a population balance model for styrene emulsionpolymerization. Close agreement was found between the model predictions and the experimental data for the number of variables which included the total number of particles formed, duration of the nucleation period, conversion at the end of the nucleation period, variation of the monomer volume fraction in the particles with conversion, and conversion–time curves for different monomer, initiator, and emulsifier concentrations.

Vale and McKenna [48] developed a mathematical model to help quantify and improve the understanding of the formation of particles and the evolution of the particle size distribution in emulsion polymerization of vinyl chloride monomer.

Almair [49] proposed a newmodeling approach for bimodal PSD in batch reactor. The parameters of the resulting model were identified using a limited set of experiments. The resulting model could then be used to produce a desired bimodal PSD.

Nadja *et al.* [50] presented an industrial semi-batch emulsion polymerization model. The model consisted of mass and energy balances and predicted the reactor temperature, conversion, the solids content and the viscosity. The model was validated on real-plant data.

Sood and Lodhi [51] developed a detailed lumped model for the emulsion polymerization of styrene. According to their extensive model discrimination study, amodel with micellar, homogeneous and coagulative nucleation mechanisms and with the Morton effect should be considered the one closest to reality.

Jung and Gomes [52] developed a dynamic mathematical model for emulsion polymerization. It included a cross-over mechanism from zero-one to pseudo-bulk kinetics and compared reasonably with experimental data for conversion, particle size and molar mass.

Sood and Singh [53] developed a simple lumped model for butyl acrylate emulsion polymerization. The model predictions were in excellent agreement with the experimental data taken from the literature for a number of variables.

Sood*et al.*[54] developed an extensive lumped model for butyl acrylate emulsion polymerization. Monomer volume in the particle was calculated based on thermodynamic considerations. Pseudo-bulk kinetics was employed to calculate the average number of radicals per particle. The model was validated against the experimental data taken from the literature.

Sood*et al.* [55] developed a simple population balance model with excellent predictive capabilities for the emulsion polymerization of butyl acrylate in a batch reactor. PSD's breadth was shown to initially broaden during the nucleation and then narrow down.

Capelli *et al.* [56] proposed the modeling and the industrial scale optimization of a polymerization process involving four monomers. The pseudo homopolymer approach together with available literature correlations for the estimation of the main constitutive parameters of the system were used to solve the mathematical model. The proposed model was validated well. Quintero *et al.* [57] proposed a reduced-order computationally-tractable multiscale model with good predictive capability.

Gaur and Sood [58] developed a comprehensive mathematical model for emulsion polymerization of butyl acrylate to polybutylacrylate in a semi-batch reactor. The population balance equations are solved using orthogonal collocation. Dynamic simulations are compared to the experimental data taken from the literature. The predictions for the various average diameters of the particle size distribution, polydispersity index, standard deviation and full particle size distribution are also given.

A computer model for the development of particle size distribution in a batch reactor for the emulsion polymerization of butyl acrylate was developed, solved and validated by Gaur and Sood [59]. The model was validated against two sets of experimental data taken from literature. The model’s reliability was demonstrated by successful simulation of the experimental data for the number of variables which included the number of particles formed at different emulsifier and initiator concentrations, the variation of conversion with time at one initiator concentration and one emulsifier concentration and number average diameter, volume average diameter at different emulsifier concentrations.

5. DISCUSSION AND FUTURE PERSPECTIVES

The area of modeling of emulsion polymerization is still growing and there are numerous potential applications of interest to both academia and industry. Models can not only provide understanding and insight into the complex mechanistic behavior of emulsion polymerization but also their validation with experimental data can reveal gaps in the knowledge where further research is required both experimentally and theoretically. Knowledge-based, validated, system-specific models of emulsion polymerization processes can simulate industrial recipes where more than one monomer is used with a variety of emulsifiers and initiators with reactors operating at non-isothermal conditions and employing different feed policies of various reaction components are still a challenge to develop, solve and validate.

NOMENCLATURE

d_M	density of monomer
$F_i(v,t)$	number of particles containing i radicals
$F(v,t)$	total number of particles
i	number of radicals per particle
$\bar{i}$	average number of radicals per particle
k_c	coagulation rate constant
k_{des}	radical exit rate coefficient
k_e	radical entry rate coefficient
k_p	propagation rate constant
k_t	radical termination rate constant
m_P	mass of polymer in a particle
MW_M	molecular weight of monomer
$[M]_W$	monomer concentration in the aqueous phase
$[M]_{W,sat}$	monomer concentration at saturation in the aqueous phase
N_A	Avogadro's Number
r	radius of particle
R_G	Universal gas constant
R_n	Rate of particle nucleation
R_v	Rate of particle growth
t	time
T	reaction temperature
v	volume of a particle
v_m	volume of a micelle
v_s	volume of a seed particle
V_R	Volume of reaction mixture

Greek Letters

γ	interfacial tension
ρ_m	density of monomer
ρ_p	density of polymer
Φ	monomer volume fraction inside the particle
χ	Flory–Huggins interaction parameter

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