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A Mathematical Model for Green Emulsion Polymerization of Methyl Methacrylate in Batch and Semi-Batch Reactors

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Abstract

*Emulsion polymerization is a **green** and **sustainable process**, as it employs **water** as the reaction medium, enables high monomer conversion at low viscosity, provides efficient heat removal, and minimizes the use of organic solvents, thereby reducing environmental impact and energy consumption. Owing to lower process temperatures, enhanced heat transfer, and the elimination **or significant reduction of volatile organic compounds**, emulsion polymerization also **contributes to reduced process-related carbon dioxide emissions, supporting pathways toward net-zero carbon manufacturing** when coupled with renewable energy sources and solvent-free downstream processing. In this work, a **mathematical model** is developed to simulate the isothermal, well-mixed **batch** and **semi-batch** emulsion polymerization of **methyl methacrylate** using a monodisperse particle size approximation. For batch operation, the model predicts the temporal evolution of monomer conversion, rate of polymerization, total particle surface area, and volume-average particle diameter at different initiator concentrations. **Model predictions** for the total number of particles **are compared with experimental data** reported in the literature, demonstrating continuous nucleation behavior. For unseeded semi-batch operation, the effects of monomer feed rate on monomer conversion and particle number are investigated. Good agreement between model predictions and experimental observations is obtained, particularly under monomer-starved operating conditions.*

Statement of Objective

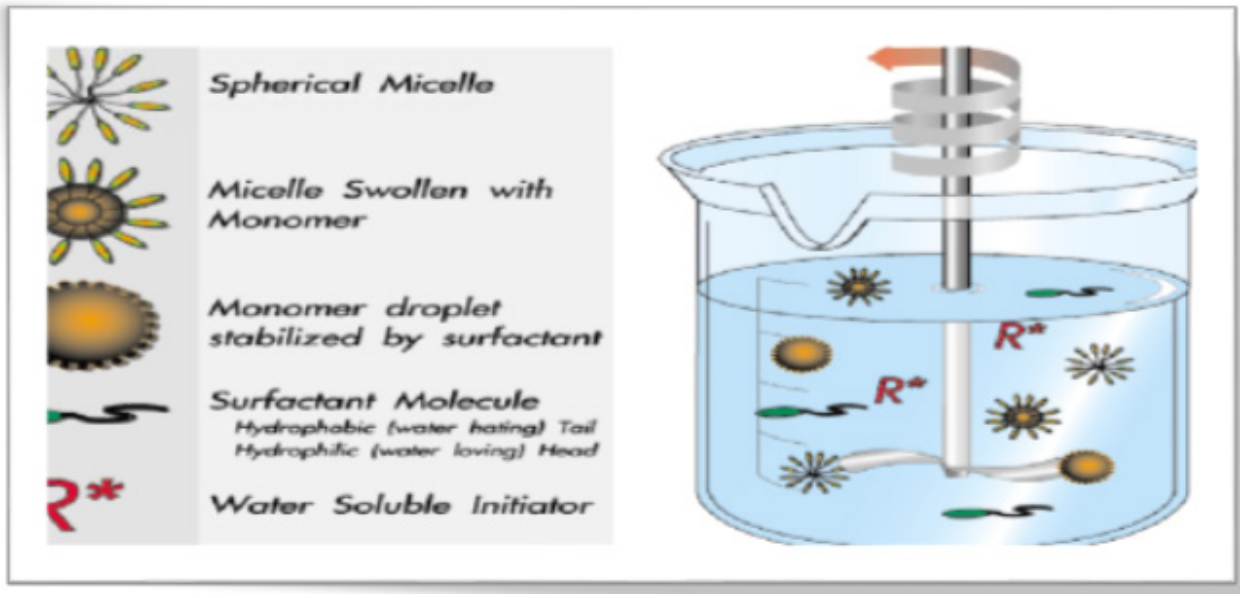
To develop a mathematical model of methyl methacrylate emulsion polymerization in batch & semi-batch reactors. Dynamic simulation results are compared to the experimental data (Gerrens (reported by Ordonez and Olayo) and Sajjadi and Yianneskis)) taken from the literatures, for the emulsion polymerization of methyl methacrylate.



Introduction to Emulsion Polymerization

- Emulsion polymerization is a process in which an aqueous dispersion of a monomer or a mixture of monomer is converted by free radical polymerization into stable dispersion of polymer particles.
- Emulsion polymerization is a large part of massive global industry. It produces high molecular weight colloidal polymers with no or negligible VOCs.
- The product of emulsion polymerization is termed as synthetic latex. Examples: styrene-butadiene rubber (SBR), polyvinyl chloride (PVC), poly methyl methacrylate (PMMA), polyvinyl acetate (PVA), acrylonitrile etc.

Recipe Ingredients



- Monomer - Methyl methacrylate
- Surfactant/emulsifier - Sodium lauryl sulfate
- Initiator - Potassium persulfate
- water

Model Development

Reaction Kinetics

Emulsion polymerization follows the kinetics of free radical emulsion polymerization, superimposed on a heterogeneous colloidal system. Free radical polymerization comprises four reaction:

1. Initiation
2. Propagation
3. Transfer
4. Termination

Initiation

Initiation, in which a primary radical (R) formed by decomposition of the initiator adds a monomer molecule (M) to form a monomer radical (M_1). Not all radicals produced by initiator decomposition initiate polymer chains.

$$\mathbf{I \rightarrow 2R}$$

$$\mathbf{R + M \rightarrow M_1}$$

$$\mathbf{R \rightarrow \text{Unreactive Products}}$$

Propagation

Propagation, in which the monomer radical adds monomer molecules successively to form a long polymer chain ending in a radical.

$$\mathbf{M_n + M \rightarrow M_{n+1}}$$

Chain Transfer

Transfer, in which a growing polymer radical abstracts a hydrogen or halogen atom from another compound (T_r) to terminate the polymer radical and form a new radical, which adds monomer molecules to grow another polymer chain.

$$\mathbf{M_n + T_r \rightarrow M_1 + P_n}$$

Termination

Termination, in which a growing polymer radical (M_n and M_m) combine to form a polymer molecule (P_{n+m}) or disproportionate to form two polymer molecules (P_n and P_m).

combination;

$$\mathbf{M_n + M_m \rightarrow P_{n+m}}$$

Disproportionation;

$$P_{n+m} \rightarrow P_n + P_m$$

Model Assumptions

- The batch & semi-batch reactors were considered to be well mixed and isothermal.
- Monodispersed particle size distribution was assumed.
- Pseudo-bulk kinetics was assumed.
- Particle coalescence was considered to be negligible.
- The micellar nucleation was followed for nucleation.

Monomer Volume Fraction in the Particle

Monomer diffusion into the polymer particles ordinarily occurs at a fast rate. Thus, one can make the quasi-state assumption that the concentration of monomer inside the particle is at its equilibrium value at all times.
The equilibrium concentration of monomer can be given by;

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

This equation is linked to the monomer balance due to the presence of monomer in the aqueous phase.

The aqueous phase monomer concentration ([M]W) can be determined by accounting for the monomer partitioning between the three phases, viz. the aqueous phase, the monomer droplets, and the polymer particles as follows;

$$[M]_R V_R = [M]_W V_W + [M]_D V_D + [M]_P V_P$$

Thus ϕ can be calculated from this equation as the monomer droplets are presents in the reactor, the aqueous phase is saturated with the monomer $[M]_W = [M]_{sat}$.
when the droplets are absent $V_D = 0$, then $[M]_W$ can be calculated from;

$$[M]_W V_W = N_{m0}(1\text{-}X) - \phi/(1 - \phi) * N_{m0} X * (\rho_m/\rho_P)$$

Here, Nm0 is the initial number of moles of monomer and X is conversion.

Average Number of Radicals per Particle

The average number of radicals per particle is determined by the rate of radical entry into, exit from, and termination inside the particle. This is given by the Smith-Ewart recursion relation;

$$k_e[F_{i-1}(v,t) - F_i(v,t)] + k_{de}[(i+1)F_{i+1}(v,t) - iF_i(v,t)] + (k_t / 2\nu N_A)[(i+2)(i+1)F_{i+2}(v,t) - i_{(i-1)}F_i(v,t)] = 0$$

The Stochmayer and O' Tool solution the above equation for the average number of radicals per particle ($i\,(v,t)$) is given by:

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

where I_b (a) is the modified Bessel function of the first kind of order b and argument a.
Where;

$$a = 4[\frac{(\nu N_a k_e)}{k_t}]^{0.5} \quad b = 4\frac{2\nu N_a k_{de}}{k_t}$$

The equation for calculating ($i\,(v,t)$) needs to be efficient because of its complexity. Several workers have expressed difficulty in evaluating the Bessel functions.

Ugelstad et al. highlighted the continued fraction form for coupling of the particle phase radical balance to the aqueous phase radical balance.

$$i = \frac{a}{4}\frac{I_b(a)}{I_{b-I}(a)} = \frac{1}{2}\frac{a^2/4}{b+}\frac{a^2/4}{b+1}\frac{a^2/4}{b+2+.....}$$

For the present work, above relation was used for calculating the average number of radicals per particle.

Overall Reactor Balances

The overall reactor balance equations include the material balances for monomer [M], polymer [P], initiator [I], and balance for the volume of reaction mixture (V_R) & number of particles formed (N_p).

The material balances, which express the rate of change of moles of each if the species in the reactor, contain accumulation, inflow and reaction terms (where appropriate). The monomer inflow term will become zero for batch reactor.

$$\frac{d[M]_R V_R}{dt} = Q_M[M]_f - R_P V_R$$

$$\frac{d[P]_R V_R}{dt} = R_P V_R$$

Where Rate of polymerization,

$$R_P = k_p \frac{\rho_M}{MW_M N_A} N_P \phi i$$

$$\frac{d[I]V_W}{dt} = -k_d[I]V_W$$

$$\frac{dV_R}{dt} = Q_M - \left(\frac{1}{\rho_M} - \frac{1}{\rho_P}\right) R_P MW_M V_R$$

$$\frac{dN_P}{dt} = R_n = k_{mm}[R]A_m$$

When $A_m > 0$ and at $A_m = 0$, $R_n = 0$

Aqueous Phase Balance

Aqueous phase balances involves the balances for the radicals, micelles, and the dissolved monomer. The equation combines the rate of radical generation in the aqueous phase, termination in the aqueous phase, entry into particles, entry into micelles and exit from the particles. A quasi- steady state assumption is used for the radical balance.

$$\mathbf{2f\, k_d\, [I] - k_{tw}\, [R]^2 - k_{mp} A_P\, [R] - k_{mm}\, A_m\, [R] + k_{de} N_{pi} = 0}$$

For the present work, termination and desorption were neglected for radical balance. So;

$$\mathbf{2f\, k_d\, [I] = k_{mm}\, A_m\, [R] + k_{mp} A_P\, [R]}$$

$$[R] = \frac{2fk_d[I]}{k_{mm}A_m + k_{mp}A_P}$$

Model Validation

Model Parameters

Methyl Methacrylate

MW_M = 100.13 g/mol
ρ_M = 0.919 g/cm^3
ρ_P = 1.19 g/cm^3
ϕ_{sat} = 0.73
M_{sat} = 1.56*10^{-4} mol/cm^3
k_p = 2.5119*10^9 exp(-22200(J)/R_GT(K) cm^3/mol s
k_{tw} = k_{t0} = 9.8*10^{10}exp(-2934.4(J)/R_GT(K) cm^3/mol s
k_t = k_{t0}*exp(-(β_1*w_P + β_2*wP^2))
β_1 = -41.54 + 0.1082*T(K)
β_2 = 23.46 – 0.0785*T(K)
k_{tr} = 3.41*10^{-5}*k_p
D_c = 1*10^{-5} cm^2/s
k_{mp} = 28 cm/s
k_{mm} = ε*k_{mp} cm/s
n = 2

Sodium Lauryl Salphate

MW_E = 288.33g/ mol
E_{CMC} = 0.0005 g/cm^3
r_m = 2.5*10^{-7} cm
$a_{em} = a_{ep} = a_{ed}$ = 50*10^{-16} cm^2

Potassium Persulphate

MW_I = 270.33 g/ mol
k_d = 1*10^{-6} s^{-1} (at 45ºC), = 1.5*10^{-6} (at 50ºC)
f = 0.5

Radical Entry Rate Coefficient

There are five different models that have been proposed for radical entry into particle: propagational entry, entry in which displacement of surfactant from the particle surface is the rate determining step, colloidal entry, diffusive entry and collisional entry.

In this work the rate of radical entry into the particle is modeled as;

$$R_{ep} = k_{mp} 4\Pi r^n N_P [R] N_A$$

The choice of n = 0 gives the propagational entry model; n = 1 gives the diffusion model for entry; while for the collisional entry model, n = 2.

In present work, a collision entry model was used.

Radical Exit Coefficient

Radical exit is generally believed to follow a transfer reaction in which small mobile free radicals formed.
Mathematical modeling of this phenomenon involves the classic concepts of diffusion with simultaneous chemical reaction.
In the present simulation studies, the following expression for the radical exit, used by Rawlings and Ray was used.

$$k_{de} = \frac{3D_c k_{tr} / k_P}{D_c M_w / k_P \phi \rho_M + r^2}$$

Gel Effect

The increase in the polymerization rate with increased monomer conversion is known as gel effect.

$k_t = k_{t0} * \exp(-(\beta_1 * w_P + \beta_2 * w_P^2))$
Where,
$\beta_1 = -41.54 + 0.1082 * T(K)$
$\beta_2 = 23.46 - 0.0785 * T(K)$
$w_P = (1-\phi) * \rho_P / (\phi * \rho_M + (1-\phi) * \rho_P)$

Model Solution

Numerical Implementation

FORTRAN programs were used to solve the modeling equations on computer.

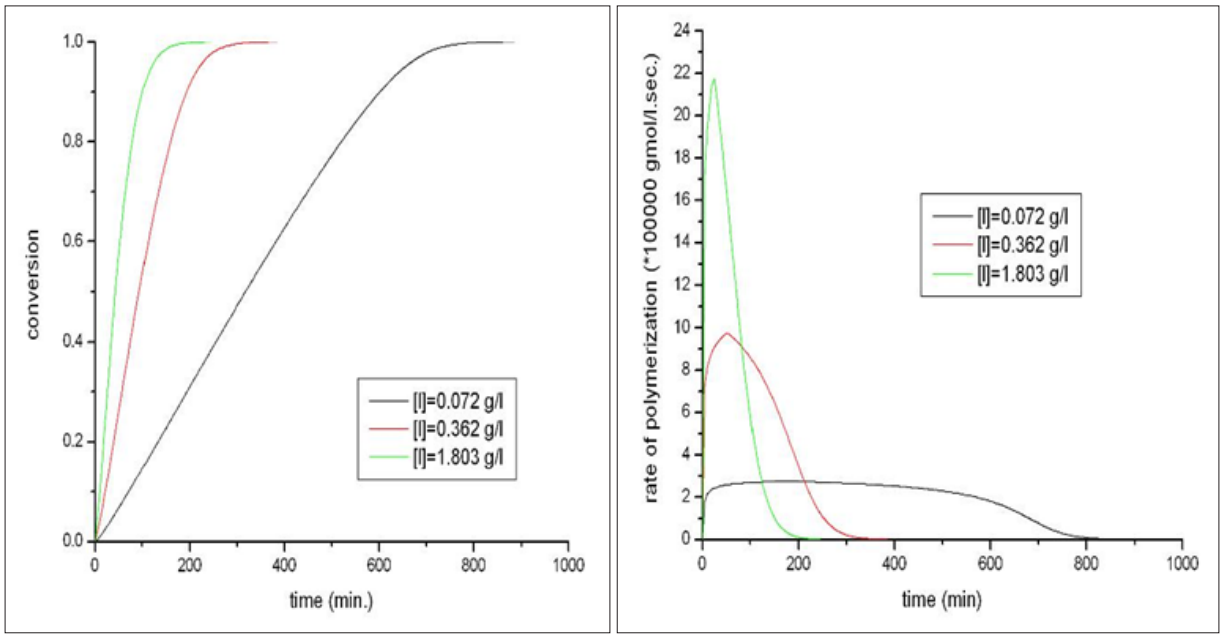
Simulation Results

- The model developed in this work was validated against the experimental data of Gerrens (reported by Ordonez and Olayo) and Sajjadi and Yianneskis.
- For the batch reactor, the amount of water taken was 1000 cm^3, the amount of monomer was 100 g and the amount of emulsifier was 5.81 g with different amounts of initiator at 45ºC.
- It was found that to provide a close match between experimental values and dynamic simulation results, the parameter ε had to be considered as an adjustable parameter.
- The value of ε decreased with increase in initiator concentration. The simulated values were close to experimental values with this adjustable parameter.

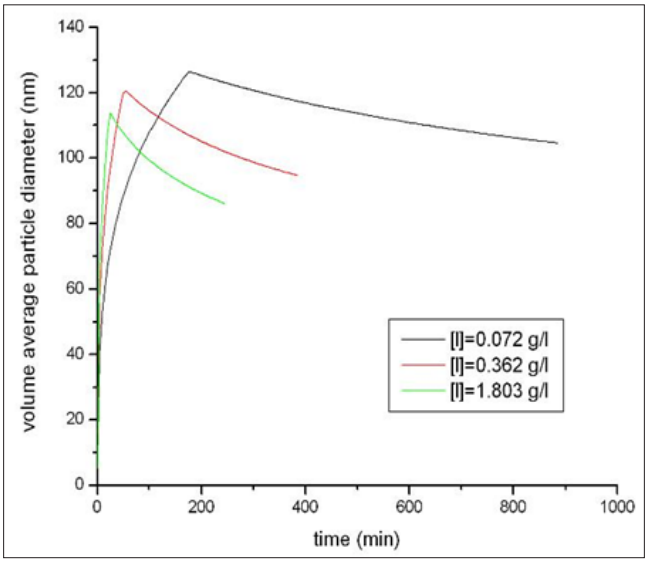
Table 1: Comparison between the experimental values and simulated values of the evolution of particles (NP) with adjustable values of parameter ε for different initiator concentrations in batch reactor.

Sr. No.	Initiator (g/L)	ε = kmm/kmp	NPExp (no./L)	NPModel (no./L)
1	0.072	0.0021	1.4×10^{17}	1.41×10^{17}
2	0.362	0.00155	1.9×10^{17}	1.90×10^{17}
3	1.803	0.00075	2.5×10^{17}	2.52×10^{17}

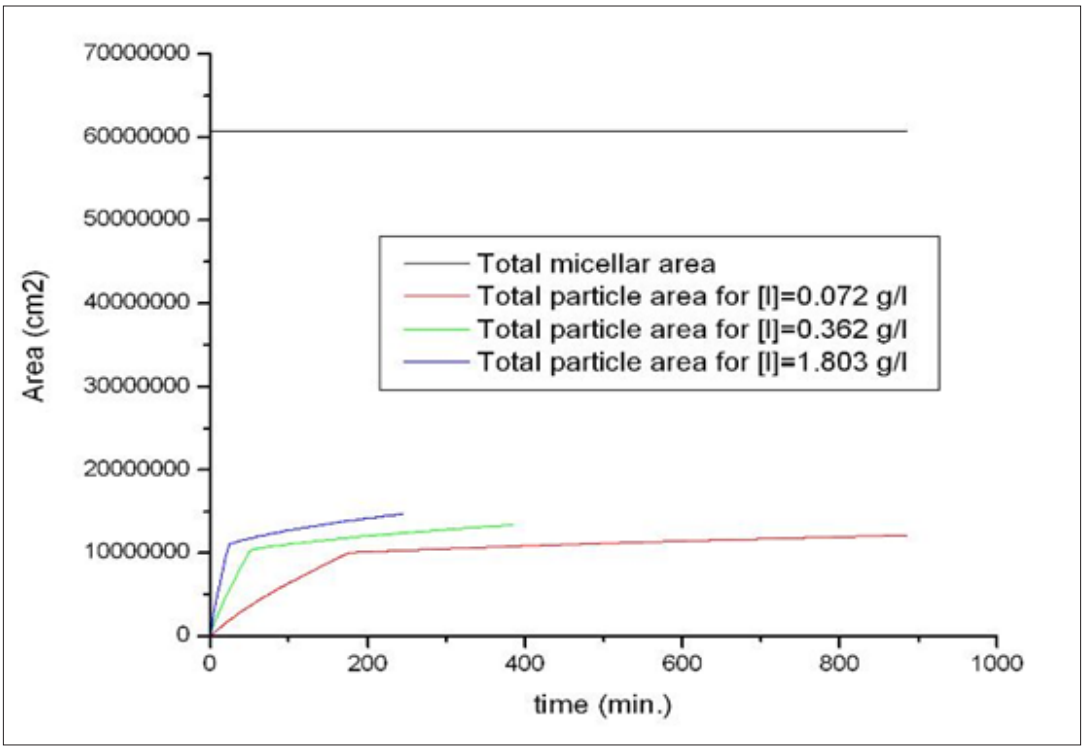
Variation of conversion & rate of polymerization with time for different initiator concentration



Variation in volume average particle diameter with time for different initiator concentration



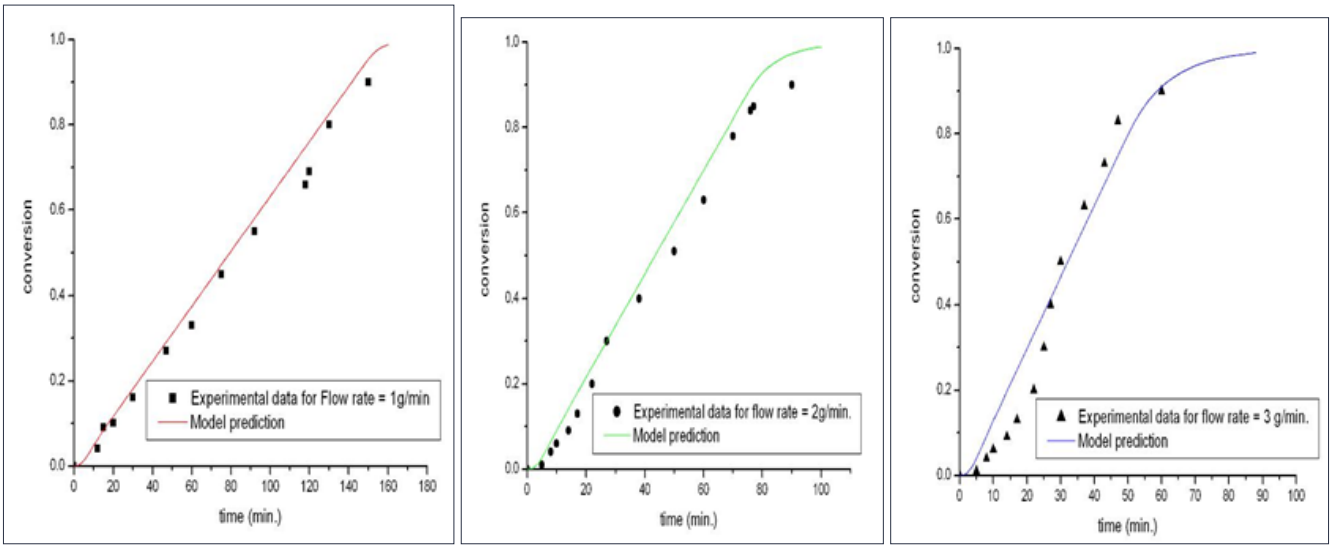
Variation in total surface area of particles as compared with total micellar area with time for different initiator concentration



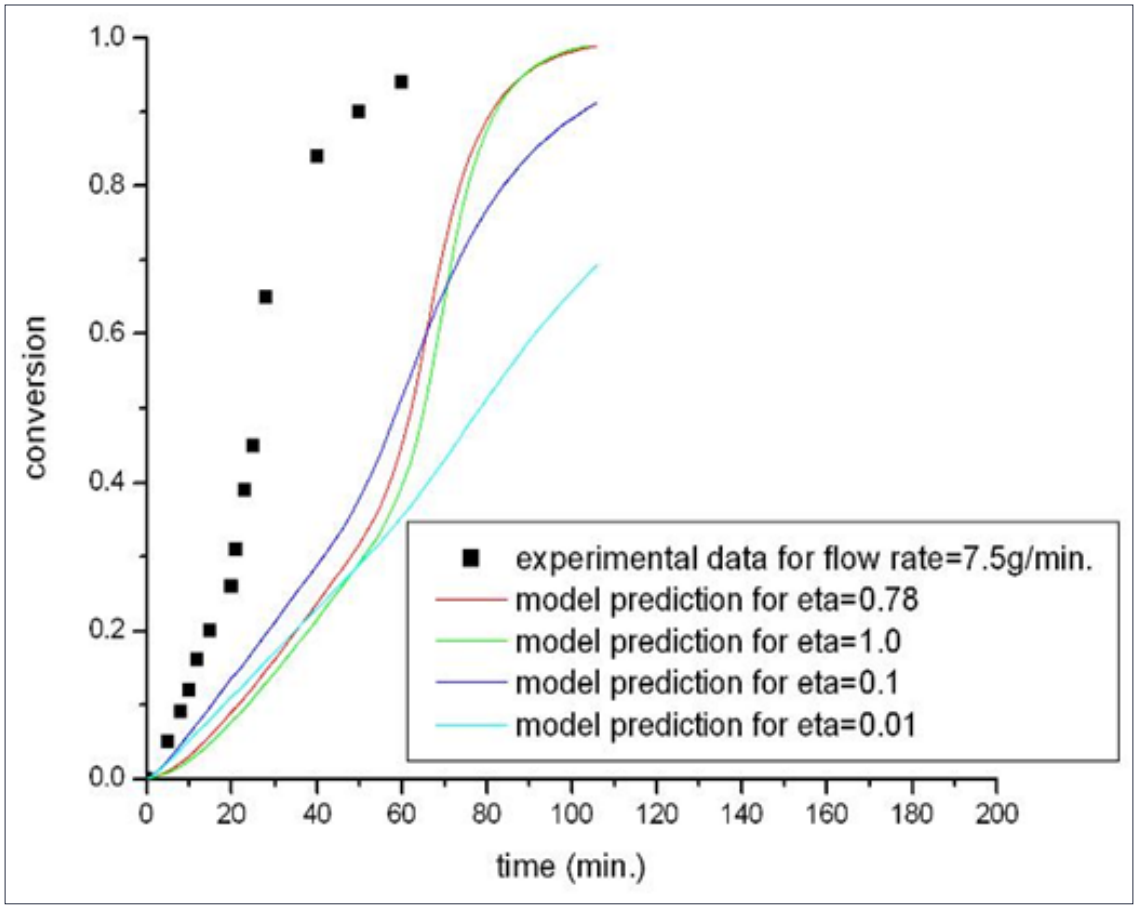
For unseeded semi-batch reactor, the amount of water was 600 cm^3, the amount of initiator (potassium persulfate) was 0.75 g, and the amount of emulsifier (SLS) was 3.0 g. The initial amount of monomer in the reactor was 0 g and the total monomer fed to the reactor was 150g at 50^0C.

It was found that to provide a close match between experimental values and dynamic simulation results for higher monomer feed flow rate, under flooded conditions, the parameter ε had to be considered again as an adjustable parameter.

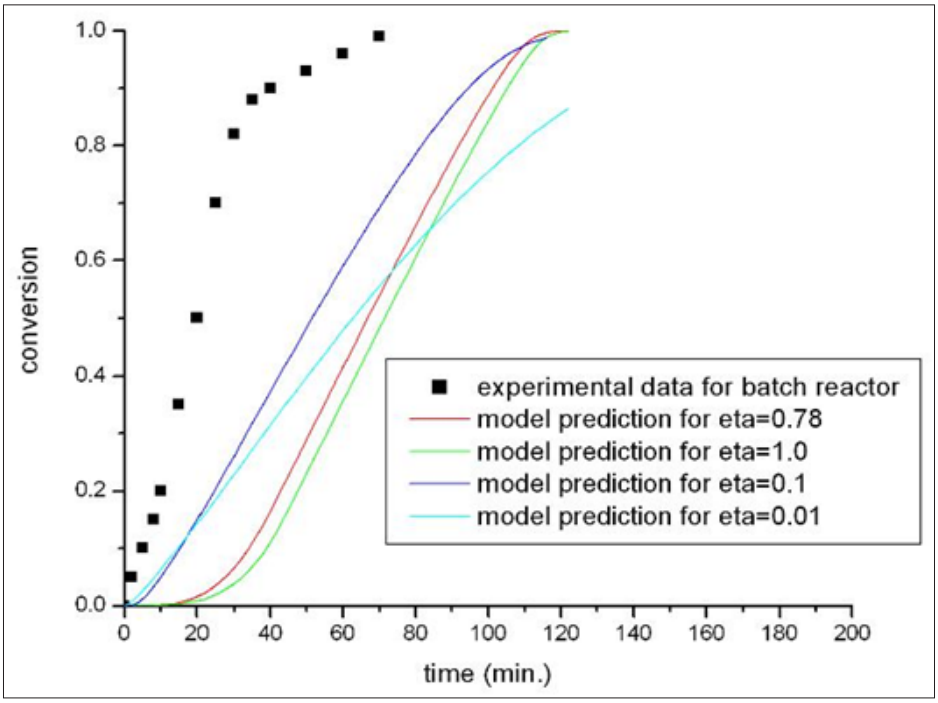
Variation of conversion with time for different feed flow rates of monomer, Ra= 1g/min, 2g/min, 3g/min



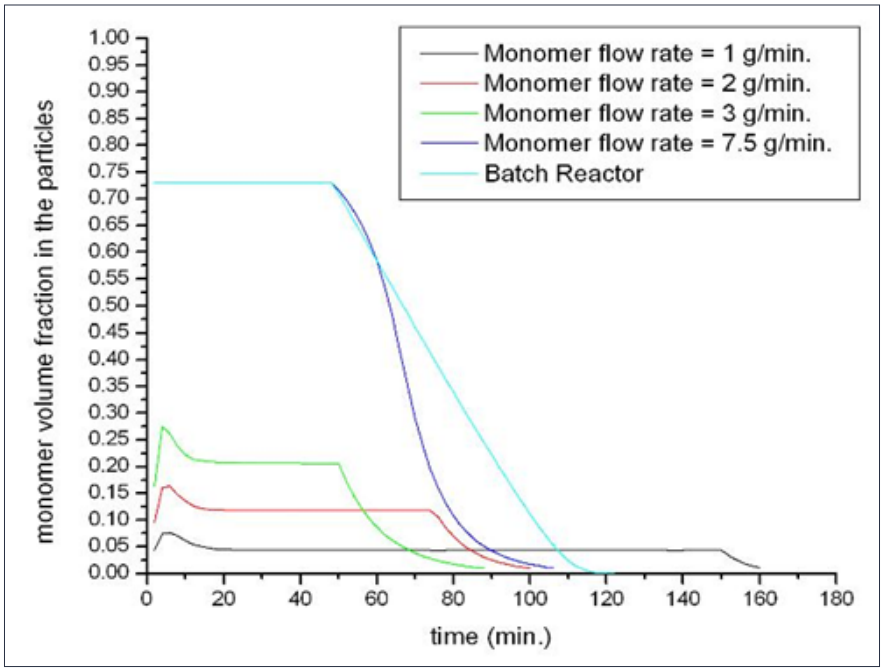
Variation of conversion with time for higher monomer feed flow rate



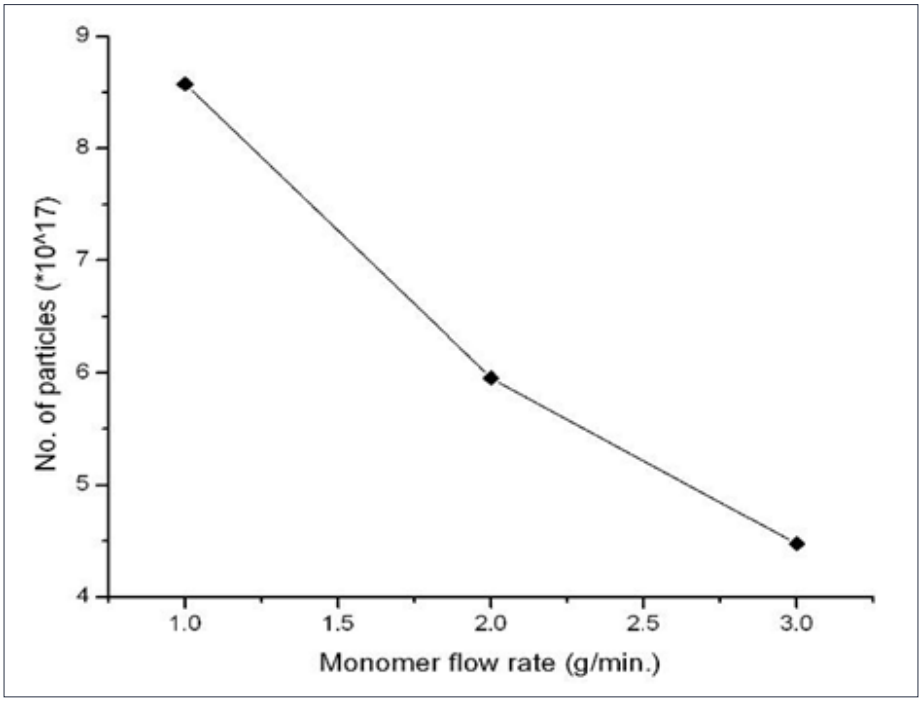
Variation of conversion with time for batch operation for various values of ε



Variation of monomer volume fraction in the particles with time, for different flow rates and the batch operation



Variation of the number of particles formed with different monomer feed flow rates in unseeded semi-batch reactor under monomer starved conditions



Conclusions

- Reasonably good agreement has been found between experimental data and simulation results.
- The model at present is applicable to batch and semi-batch reactors. It should be extended to continuous reactors also.
- It should be also extended to the model for polymerization of other monomers such as vinyl acetate etc.
- The model should include homogeneous nucleation.
- The model should account for the full particle size distribution.
- Main motivation for this study is to promote the use of eco-friendly polymer products for sustainable development.

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