Modeling of emulsion copolymerization reactors: from kinetics and thermodynamics to the dispersion stability

Control and Real-time Optimisation of Intensive Polymerisation

FP7-NMP-2011-Small-5 Grant Agreement 280827

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14. January 2015
Frankfurt, Germany
Motivation

• Concept of the COOPOL project:
  – develop robust real-time optimization-based control and sensing methodologies

• Our goals:
  – develop mathematical models for both existing semi-batch and emerging ‘smart-scale’ (e.g. continuous) processes
Strategy to achieve our goals

• Starting point:
  – Models of emulsion copolymerization previously developed (i) by our group\(^{(A)}\), and (ii) by group of prof. Engell at TUD\(^{(B)}\)

• Adaptation and improvement of models to our problem:
  – semi-batch: 4 monomers (two of them water soluble), seed
  – smart-scale: 2 monomers (insoluble in water), unseeded

• Model reduction – models suitable for on-line process control (robust and fast)

Presentation outline

• 1) Process model for **semi-batch polymerization**
  – 4-monomer system: 2 hydrophobic + 2 water-soluble
  – Complex monomer partitioning
  – pH dependency of polymerization rate (dissociation)

• 2) Process model for polymerization in **smart-scale reactor**
  – Unseeded polymerization – nucleation of particles
  – Small particles: Monomer partitioning based on Morton equation

• 3) Innovative use of sensors
  – on-line **information about cross-linking**

• 4) Modeling of **coagulation/fouling** dynamics
  – Predicting the boundaries for safe (coagulum free) operation

**SKIPPED**
Semi-batch reactor modeling

- Monomer-starved conditions
- Hydrophobic (M1,M3) + hydrophilic (M2,M4) comonomers
- Need to **quickly** and **accurately** predict:
  - Conversion of monomers
  - Solid content
  - Polymer MWD
Semi-batch reactor modeling

- Separation of reaction medium into:
  - Emulsion copolymerization (M1+M3) in polymer phase.
  - Solution copolymerization (M2+M4) in water.

- Model formulated as system of ODE based on:
  - Material balance of non-polymeric species in all phases.
  - Material balance of radicals in polymer and aqueous phase.
  - Population balance of polymer moments (summed over polymer and aqueous phase).
  - Heat balance of reaction mixture and cooling jacket.
Semi-batch reactor modeling

• Kinetic scheme involves:
  – Initiation + propagation.
  – Termination (combination/disproportionation).
  – Chain transfer to monomer and mercaptan.
  – Intramolecular chain transfer (backbiting) → SCB.

• Model validated by 15 laboratory experiments for:
  – Individual conversion of all monomers.
  – Solid content in the emulsion.
  – Average molecular weights of produced polymer.
Semi-batch reactor modeling

Instantaneous conversion of individual monomers

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Semi-batch reactor modeling

Average molecular weights of polymer

Total conversion, solid content
„Smart-scale“ reactor modeling

• Next to the model of semi-batch reactor, we also develop model for the emulsion polymerization in smart-scale reactor (basically continuous tubular reactor)

• Low investment costs – polymers for special applications

Courtesy of Fabian Lueth
University of Hamburg
„Smart-scale“ reactor modeling

• Modelled as axially dispersed plug-flow reactor using method of lines (MOL)

• Balance equations for state variables $\psi$
  
  – Monomers, polymer, water, initiator, emulsifier, average number of radicals per particle, number of particles ($\psi = c_{Mi}, c_P, \phi_w, c_I, n_{AVG}, N_T$)
  
  \[
  \frac{\partial \psi}{\partial t} + v \frac{\partial \psi}{\partial z} - D_e \frac{\partial^2 \psi}{\partial z^2} = \sigma
  \]

• Danckwerts boundary conditions:
  
  \[
  \frac{D_e}{v} \frac{\partial \psi}{\partial z} = \psi - \psi_e \quad z = 0
  \]
  
  \[
  \frac{\partial \psi}{\partial z} = 0 \quad z = L
  \]
Validation – conversion, comonomer content, Mw, Mn
Using the same kinetic parameters as in semi-batch
First simulations revealed slower reaction rate at the beginning of the reactor
  – nucleation implemented, but found to be almost instantaneous

Possible cause – thermodynamics of monomer partitioning
Monomer partitioning

- Implementation of non-linear Morton-Kaizerman-Altier equation for the monomer partitioning
- Equilibrium of chemical potentials in all phases
- Lower monomer fractions in small particles – slower reaction

\[
\frac{\Delta G_{i,polymer}}{RT} = \ln(1 - \phi_p) + \phi_P + \chi_i \phi_P^2 + \frac{2\sigma V_{m,i}}{R T r_P} + \frac{V_m \rho_P}{M_C} \left( \phi_P^{1/3} + \phi_P \right)
\]
Monomer partitioning

- MKA equations are highly nonlinear, the integration needs a good initial guess and considerably slows down the calculations in the process model of tubular reactor
  - Empirical relationship used to predict volume fraction of monomers in polymer $\phi_i^P$ as a function of process conditions and parameters
  \[
  \phi_i^P = a_{i,1} \left[ a_{i,2} \sigma + \arctan \left( \frac{r_p}{a_{i,3}} \right) \right] \frac{k_i^P}{k_i^D} \phi_i^D
  \]

- Comparison of MKA solution (colored surface) with surrogate model (black surface)

$r_p$ \hspace{1cm} particle radius
$\sigma$ \hspace{1cm} interfacial tension
$T$ \hspace{1cm} temperature
$\phi_i^D$ \hspace{1cm} volume fraction of monomer in droplets
$k_i^P$ \hspace{1cm} partitioning coefficient between polymer and water
$k_i^D$ \hspace{1cm} partitioning coefficient between polymer and droplet
Monomer partitioning

- Implementation of non-linear Morton-Kaizerman-Altier equation for the monomer partitioning

- Excellent agreement

![Graph showing conversion and mean residence time](image)
Monomer partitioning - results

- Comparison for different STY/BA ratios (30 wt.% monomer)

  - Copolymer composition
    - Excellent agreement

  - Molecular weight
    - reasonable agreement in number-average molecular weight
Stabilized dispersions are encountered in various applications

- Food, cosmetics, etc.
- Emulsion & suspension polymerization
Motivation – Coagulation

- Stabilized dispersions are encountered in various applications
  - Food, cosmetics, etc.
  - Emulsion & suspension polymerization
- Coagulation may cause serious financial losses

Coagulum in an industrial reactor

TubeTech International, Ltd.
Stabilized dispersions are encountered in various applications:
- Food, cosmetics, etc.
- Emulsion & suspension polymerization

Coagulation may cause serious financial losses.

Proper understanding of the coagulation mechanism is crucial for the operation of industrial units.

Coagulation kinetics

Characteristic coagulation time $t_c$ vs. shear rate $G$

- $\phi = 0.19$
- $\phi = 0.21$
- $\phi = 0.23$

Development of a predictive model of coagulation

- Coagulation & fouling – complex phenomena
- Model accounting for all effects is needed

Bulk stability

Size of clusters

Interactions with wall

Interactions with flow
Advantages of the DEM model

• Large number of particles (currently 5000)
  – Enables modeling of **crowded systems**
  – Captures interactions between **many clusters** instead of simulations with a single cluster

• Direct incorporation of inter-particle forces
  – Our model describes interaction of particles that are **elastic, adhesive** and **stabilized**
  – Particle-fluid interaction is modeled by two-way coupling
Stability of dispersions

- In concentrated dispersions, individual collisions are no longer independent.
- How is then the coagulation kinetics computed?

\[
\varphi \approx 0.50 \quad \varphi \approx 0.05
\]
Discrete Element Method (DEM)

- Particles described as discrete elements
  - Newton's second law
    \[ \frac{d^2 x}{dt^2} = \frac{F}{m} \]
    \[ \frac{d\Omega}{dt} = \frac{M}{I} \]
  - Angular momentum balance

- Normal interactions – connection of DLVO & JKR theory
- Tangential interactions
  - Sliding, rolling, twisting
- Model of simple shear

![Diagram of particle separation and potential energy](image)

- Elasticity
- Stabilization
- Adhesion

Potential energy \( U / k_B T \) vs. Particle separation distance \( h / \text{nm} \)
Initial setup

- A concentrated system
- Initially, particles are placed in a “safe” distance, such that no interaction occurs.

### Parameters of the system

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<th>Value</th>
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<td>$R_p$</td>
<td>50 nm</td>
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<tr>
<td>$\rho_p$</td>
<td>1000 kg·m$^{-3}$</td>
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<tr>
<td>$A_H$</td>
<td>$1.3\cdot10^{-20}$ J</td>
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<tr>
<td>$\kappa^{-1}$</td>
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<tr>
<td>$\psi_0$</td>
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<tr>
<td>$E_Y$</td>
<td>40 MPa</td>
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<tr>
<td>$\gamma$</td>
<td>3 mJ·m$^{-2}$</td>
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Results – coagulation dynamics

- Coagulation in stabilized systems – activated process
- Fast aggregate growth occurs after initial lag-phase.

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- Coagulation in stabilized systems – activated process
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Characteristic coagulation time

Particle volume fraction $\phi$

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Coagulation dynamics - doublet formation

- Doublet formation – approx. two orders of magnitude slower than the coagulum formation

![Graph showing characteristic coagulation time vs. shear rate](image)
Size of the resulting clusters

- 3D model needed to fully capture structure of clusters
- Particle volume fraction $\varphi = 0.05$
- Initial setup: non-agglomerated system

Radius of gyration ($2R_g$)
Size of the resulting clusters

- 3D model needed to fully capture structure of clusters
- Particle volume fraction $\varphi = 0.05$
- Initial setup: non-agglomerated system

Non-stabilized system

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<td>$\psi_0$</td>
<td>0 mV</td>
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<tr>
<td>$E_Y$</td>
<td>1000 MPa</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.3 mJ·m$^{-2}$</td>
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Coagulation in non-stabilized system (no energy barrier)
- At the beginning controlled solely by coagulation
- The final size of aggregates is the result of interplay between coagulation and breakage
Size of clusters – non-stabilized

- Coagulation in non-stabilized system (no energy barrier)
- At the beginning controlled solely by coagulation
- The final size of aggregates is the result of interplay between coagulation and breakage

Slope of the fitted lines:
\[ p = 0.64 \pm 0.03 \]

Theoretical scaling:
\[ p = 0.66 \]

Surface energy \( \gamma \) (mJ·m\(^{-2}\))

For fractal dimension \( d_f = 2.7 \)
Future work

- Detailed study of the **particle-wall** interactions

- Simulations of **fouling** in a micro-channel
Summary

- Coagulation of stabilized dispersions was modeled using the Discrete Element Method (DEM).
- Simulations showed strong dependence of coagulation time on volume fraction and shear rate.

Characteristic coagulation time

Number of particles in aggregates vs. time

Characteristic coagulation time vs. shear rate

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Autocatalytic nature of coagulation requires detailed modeling to capture its complicated kinetics.

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Simulations showed strong dependence of coagulation time on volume fraction and shear rate.

Autocatalytic nature of coagulation requires detailed modeling to capture its complicated kinetics.

Size of the resulting clusters is determined by coagulation and breakage, and depends on surface energy.
Conclusions – model development

• Models for both semi-batch and smart-scale reactors were developed and validated by laboratory data

• Models are currently implemented for on-line control of real pilot-plant reactors

• First-principle mathematical model of coagulation developed to predict characteristic coagulation time – now being adapted for use in real systems
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