Modeling and Parameter Estimation of Interpenetrating Polymer Network Process

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Interpenetrating Polymer Network Process

Fig 1. Seed Polymerization Process
Overview

Objective: **Optimization**

Tool: **Modeling**

**Parameter Estimation**

**Control Optimization**

- Macroscale
- Mesoscale
- Microscale
## Previous Work Review – New Model Development

**Components**
- **Continuous phase**
  - Water
  - Water, Water-soluble initiator
  - Monomer (+ Inert hydrocarbon diluents)
- **Dispersed phase**
  - Monomer/Polymer droplets, Suspension agent, Oil-soluble initiator
  - Monomer droplets, Latex particles, Emulsifier
  - Formed polymer particles with catalysts sites
- **Reaction sites**
  - Monomer/Polymer Droplets
  - Latex particles
  - Surface of the catalysts supporter
- **Kinetics**
  - Similar to bulk
  - Compartmentalisation
  - Heterogeneous
- **Particle evolution**
  - Coalescence/breakup
  - Homogeneous and micellar nucleation
  - Growing polymer layers around active sites
  - Growing new polymer penetrating the seeds

### Table 1. Special Features of IPN particle growth

<table>
<thead>
<tr>
<th>Semi-batch suspension polymerization (SSP)</th>
<th>Seeded emulsion polymerization (SEP)</th>
<th>Supported Catalyst Polymerization (SCP)</th>
<th>Seed polymerization (SP)</th>
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Single Particle Modeling

- Particle growth mechanism
- Intra-particle diffusion
- Dynamics of the kinetics

- Based on mass conservation law
  \[
  \frac{dN_i^{[k]}}{dt} = N_i^{[k] \text{In}} - N_i^{[k] \text{Out}} + N_i^{[k] R}
  \]

- External mass transfer
  - Collision absorption assumption
    \[
    \dot{N}_{i \text{ns}}^{in} = \frac{TF_i(t)}{N_{\text{seed}}}
    \]

- Internal mass transfer
  - Fick’s first law approximation
    \[
    \dot{N}_{i+1}^{[k] \text{Out}} = \dot{N}_i^{[k] \text{In}} = \dot{S}_i \cdot J_i
    \]
    \[
    J_i = D \nabla C_i = D \frac{\partial C}{\partial r}|_i = D \frac{dC}{dr}|_i
    \]

- Local reaction rate
  \[
  K_t^{[k]} = K_{t0} \cdot Gel(x_s^{[k]} \cdot T)
  \]
New Improvement (1)

• Modeling Particle growth
  – Partial molar Volume model
    \[ V_{[k]} = \sum_j n_j[k] \bar{V}_j[k] \] Partial molar properties of j
  • Concentration dependent approximation \[ \bar{V}_l = a_0^l + a_1^l \cdot C_M \]
  • Shell volume representation
    \[
    V_{[k]} = N_{M}^{[k]} \bar{V}_{Mb} + N_{P}^{[k]} \bar{V}_{Pb} + N_{A}^{[k]} \bar{V}_{A} \]
    \[
    = N_{M}^{[k]} (a_0^S + a_1^M \bar{C}_{Mb}) + N_{P}^{[k]} (a_0^{Pb} + a_1^{Pb} \bar{C}_{Mb}) + N_{A}^{[k]} (a_0^A + a_1^A \bar{C}_{Mb}) \]
  – Initial condition estimation
    • Initial conversion / molecular weight
      ◡ 13 system parameters + 2/process initial condition
Parameter Ranking and Subset Selection (1)

\[ \tilde{y} = y(\theta) + \epsilon \]
\[ \tilde{y} = [\tilde{y}(t_1), \ldots, \tilde{y}(t_n)]^T \] is the observation of the output,
\[ y(\theta) = [y(t_1, \theta), \ldots, y(t_n, \theta)]^T \] is the true value,
\[ \epsilon = [\epsilon(t_1), \ldots, \epsilon(t_n)] \] is the measurement noise.

\( \epsilon \) follows Gaussian distribution with zero mean and a covariance matrix \( \Sigma \).

**Fisher Information Matrix:**

\[ F(\theta) = E \left[ \frac{\partial}{\partial \theta} \ln p(\tilde{y}|\theta) \left( \frac{\partial}{\partial \theta^T} \ln p(\tilde{y}|\theta) \right) \right] = \left( \frac{\partial y}{\partial \theta} \right)^T \Sigma^{-1} \frac{\partial y}{\partial \theta^T} \propto S^T S \]

**The Cramer Rao inequality:**

\[ \text{var} \hat{\theta} \geq tr(F)^{-1} \]

Parameter Ranking

\[ SE = QR \]

Subset selection

\[ R = D \tilde{R}, \quad (E^T S^T SE)^{-1} = UD^{-2} U^T \]

\[ U = \tilde{R}^{-1} \] unit upper diagonal.

\[ \Delta \text{var} \hat{\theta}_j = \frac{||u_j||^2}{d_j^2} \]

[Lund, B; Foss, B, Automatic 2008, 44(1), 278-281]
Parameter Ranking and Subset Selection (2)

Multi-response sensitivity coefficient matrix

\[ S = \begin{bmatrix}
\frac{\theta_1^* \partial y_1}{y_1^* \partial \theta_1} | t=t_1 & \cdots & \frac{\theta_P^* \partial y_1}{y_1^* \partial \theta_P} | t=t_1 \\
\vdots & \ddots & \vdots \\
\frac{\theta_1^* \partial y_R}{y_R^* \partial \theta_1} | t=t_1 & \cdots & \frac{\theta_P^* \partial y_R}{y_R^* \partial \theta_P} | t=t_1 \\
\vdots & \ddots & \vdots \\
\frac{\theta_1^* \partial y_R}{y_R^* \partial \theta_1} | t=t_N & \cdots & \frac{\theta_P^* \partial y_R}{y_R^* \partial \theta_P} | t=t_N
\end{bmatrix} \]

- 3 types of measurements
  - Molecular weight
  - Conversion ratio
  - Particle size
- 3 grades of products
- 19 model parameters

\((\theta_1, \cdots, \theta_P)\) is a set of parameters to be estimated,
\((y_1, \cdots, y_R)\) is a set of responses,
\(\theta_i^*, y_i^*\) are the reference values of \(\theta_i\) and \(y_i\),
\((t_1, \cdots, t_N)\) is a set of selected sample points in time.
Combine the parameter ranking information with the simultaneous estimation strategy.

**Tab 2: Result of Parameter Selection and Estimation**

<table>
<thead>
<tr>
<th>Ranked Parameter</th>
<th>$\Delta \text{var} \hat{\theta}_i$</th>
<th>Estimated value for $N_p$ parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p$</td>
<td>0.017</td>
<td>1.05(±0.054) 1.05(±0.053) 1.07(±0.047)</td>
</tr>
<tr>
<td>$x_{s0}^{(r)}$</td>
<td>0.134</td>
<td>1.07(±0.011) 1.07(±0.011) 1.06(±0.010)</td>
</tr>
<tr>
<td>$a_{s0}^{(r)}$</td>
<td>0.167</td>
<td>0.83(±0.440) 0.81(±0.078) 0.87(±0.066)</td>
</tr>
<tr>
<td>$f$</td>
<td>0.270</td>
<td>0.76(±0.089) 0.76(±0.088) 0.82(±0.078)</td>
</tr>
<tr>
<td>$x_{s0}^{(m)}$</td>
<td>0.393</td>
<td>1.28(±0.011) 1.28(±0.011) 1.28(±0.010)</td>
</tr>
<tr>
<td>$x_{s0}^{(m)}$</td>
<td>0.495</td>
<td>1.33(±0.021) 1.33(±0.021) 1.33(±0.020)</td>
</tr>
<tr>
<td>$M_{w0}^{(r)}$</td>
<td>0.498</td>
<td>0.70(±0.24)  0.71(±0.23)  0.66(±0.21)</td>
</tr>
<tr>
<td>$M_{w0}^{(m)}$</td>
<td>0.845</td>
<td>1.24(±0.23)  1.26(±0.23)  1.17(±0.22)</td>
</tr>
<tr>
<td>$M_{w0}^{(m)}$</td>
<td>0.981</td>
<td>1.13(±0.50)  1.14(±0.41)  1.15(±0.30)</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>1.310</td>
<td>0.84(±0.26)  0.98(±0.12)  0.91(±0.11)</td>
</tr>
<tr>
<td>$\alpha_{ps}$</td>
<td>3.611</td>
<td>2.01(±0.35)  1.90(±0.18)  1.78(±0.14)</td>
</tr>
<tr>
<td>$\alpha_0^p$</td>
<td>6.117</td>
<td>0.92(±0.41)  0.47(±0.30)</td>
</tr>
<tr>
<td>$\alpha_1^4$</td>
<td>23.332</td>
<td>0.11(±1.07)</td>
</tr>
<tr>
<td>$K_{fs}$</td>
<td>69.192</td>
<td></td>
</tr>
<tr>
<td>$a_{ps}$</td>
<td>134.449</td>
<td></td>
</tr>
</tbody>
</table>
New Estimation Results

Fig 4. Fitting results for Three Grades of Products
New Improvement (2)

• Kinetics of Multi-polymer System

• Key Concern of the Model: Model complexity
  – Multiple reaction probability distributions from model sources
  – Highly nonlinear structure
  – Difficulties for efficient optimization
Possible Reactions in IPN System

Grafting
Intermolecular transfer
Network
β- scission

Fig 5. Schematic Representation of the Nonlinear Reactions in the IPN System

Free radical on chain B
Free radical on chain A
Grafted polymer
Crosslinked polymer
Nonlinear Polymer Molecular Weight Calculation

- Numerical fractionation
- Instantaneous MWD method
- Discrete weighted residuals
- Approximation functions of molecular weight distribution
- Monte Carlo simulation
- Double moment method
- Population balance approach

Unable to model chain random scission
Difficult to optimization
Has not applied for polymer composite system
Decompose the Nonlinear Structure

Separate representation for two polymers

\[ A^* B = A^* + GD_B \]
\[ AB^* = A + GP_B \]

**Chain initiation:**
\[ R^* + A(m) \xrightarrow{k_2} A^*(m) \]

**Propagation:**
\[ A^*(m) + M \xrightarrow{k_p} A(m) + GP^1_B \]

**Chain transfer:**
\[ P^i_B + A(m) \xrightarrow{k_{fb}} D^i_B + A^*(m) \]
\[ GP^i_B + A(m) \xrightarrow{k_{fb}} GD^i_B + A^*(m) \]

**Intramolecular transfer:**
\[ A^*(m) \xrightarrow{k_{bi}} A^*(m) \]

**\(\beta\)-scission:**
\[ A^*(n) \xrightarrow{k_\beta} A^*(x) + A(n - x) \]

**Termination:**
\[ A^*(m) + A^*(n) \xrightarrow{k_{ta}} A(m + n) \]
\[ A^*(m) + A^*(n) \xrightarrow{k_{td}} A(m) + A(n) \]
Statistical and Sectional Grid Approach (1)

analogy to
Chain combination / breakup \leftrightarrow Particle breakup / aggregation

- Sectional grid approach – Fixed pivot technique

\[
\begin{align*}
&n_1 & n_2 & n_2 & n_4 \\
x_1 & x_2 & x_3 & x_4 & x_5
\end{align*}
\]

Chain length between \([x_i, x_{i+1}]\) is represented by \(n_i\), where \(n_i = \frac{1}{2}(x_i + x_{i+1})\)

Two properties are preserved by assigning chain length \(x\) to populations at \(x_{i-1}, x_i, x_{i+1}\)

\[
\begin{align*}
& a(v, x_i) f_1(x_i) + b(v, x_{i+1}) f_1(x_{i+1}) = f_1(v) \\
& a(v, x_i) f_2(x_i) + b(v, x_{i+1}) f_2(x_{i+1}) = f_2(v)
\end{align*}
\]

(Number and mass are preserved by set \(f(v)\) to zeroth and first properties)
Statistical and Sectional Grid Approach (2)

- Chain random scission:
  \[ R_i = \sum_{k=i}^{M} n_{i,k} N_k(t) \]

  \( M \): Number of sectional grids
  \( n_{i,k} \): Contribution to population at \( i^{th} \) representative chain length due to the breakage of a chain of chain length \( x_k \)

  For preservation of total number and mass of polymer chain

  \[ n_{i,k} = \int_{x_i}^{x_{i+1}} \frac{x_{i+1} - v}{x_{i+1} - x_i} \beta(v, x_k) dv + \int_{x_{i-1}}^{x_i} \frac{v - x_{i-1}}{x_i - x_{i-1}} \beta(v, x_k) dv \]

  \( \beta(x, x_k) \): Break up kernel function

  Possibility of length of \( x_k \) chain to break into length of x chain
Chain combination:

\[ R_i = \sum_{j \geq k} (1 - \frac{1}{2}\delta_{j,k}) \eta Q_{j,k} N_j t N_k(t) \]
\[ x_{i-1} \leq (x_j + x_k) \leq x_{i+1} \]

For preservation of total number and mass of polymer chain

\[ \eta = \begin{cases} \frac{n(i+1) - n}{n(i+1) - n(i)} & n(i) \leq n \leq n(i+1) \\ \frac{n - n(i-1)}{n(i) - n(i-1)} & n(i-1) \leq n \leq n(i) \end{cases} \]

where \( n = n(j) + n(k) \)

\[ Q_{j,k} = Q(x_j, x_k): \text{Aggregation kernel function} \]

Possibility of length of \( x_k \) live chain and length of \( x_j \) live chain to form length of \( x_{j+k} \) dead chain
Statistical and Sectional Grid Approach (4)

• Nonlinear chain structure is recovered by statistical assemblage
  – Position independent assumption

• Network fraction is classified by crosslinked chain length

New model capabilities

- Gel fraction / Gel composition
- Branching frequency
- Joint molecular weight distribution
Summary

• Single particle model has been improved in modeling particle growth
• Consistent agreement was observed in all studied cases
• Parameter ranking and subset selection are implemented for parameter estimation
• Kinetics of polymer composite is under study. More efficient modeling approach is proposed for further research