Model-based experimental analysis for inter-polymer process

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Outline

- Project overview
- Primitive model construction
- Model refinement and existing challengesFuture work and conclusion

Project overview

Model-based experimental analysis

□ The link between experiment and industry process



- □ Kinetic modeling is a key technology
 - Design, control, operation of manufacturing process
 - Better understand of the micro-scale phenomena in chemical systems





Project overview

Model-based experimental analysis for interpolymer process

- Objective --- Model-Based experimental design
- □ Challenge --- Complex kinetic mechanism
- □ Major questions were raised
 - How to build an initial model
 - How to solve the inverse problem
 - How to evaluate the model
 - How to implement the experimental design

Primitive model construction(1) Reduce the complexity of the Inter-polymer system

Active unit concept



Compact kinetic model scheme (Free radical Polymerization)





Primitive model construction(2) Inverse approach for parameter estimation



Arrhenius equation
$$K = A e^{-E_a/RT}$$

Apparent kinetic reaction rates •Gel effect •Glass effect •Cage effect

Parameter-estimation-assisted

$$K(t_1), K(t_2), K(t_3), K(t_4) \bullet \bullet \bullet$$
$$\longrightarrow K(time) \longmapsto K(X)$$

Primitive model construction(2) Inverse approach for parameter estimation (Cont.)

Compute implementation

Convergence and robustness problems of the nonlinear estimation algorithms

Min.
$$\sum_{u} \sum_{j} e_{ju}^{2}$$

S.t.
$$f\left(\frac{dx}{dt}, x, y, t\right) = 0$$
$$x_{L} \le x \le x_{U}$$
$$y_{L} \le y \le y_{U}$$
$$f\left(\frac{dx}{dt}\Big|_{t=0}, x(0), y(0), 0\right) =$$

0.

Simultaneous approach

Discretize all the variable in time at Radau collocation points

$$y(t) = y_{i-1} + h_i \sum_{q=1}^{NC} \Omega_q(\frac{t - t_{i-1}}{h_i}) \frac{dy}{dt_{i,q}}$$

Enforce continuity at each finite element

$$y(z) = y_{i-1} + h_i \sum_{q=1}^{NC} \Omega_q(1) \frac{dy}{dz_{i,q}}$$

Solved as large scale nonlinear optimization problem (IPOPT)

var. \geq 3,000 In each sub-model

Primitive model construction (2) Inverse approach for parameter estimation (Cont.)



Primitive model construction (3) Hybrid methods for property simulation

Molecular weight distribution / Network fraction

0.8

0.7

0.6 0.5

0.3 ₩ 000 0.4 ₩ 0.3

0.2

0.1

0

0.5

1

1.5 2

Log (Molecularweight)

25

3



Step 1: Separated Molecular weight distribution

The method of finite molecular weight moments



35

Quasi-steady-state assumption to live polymer

$$L_i = (1 - \alpha)L\alpha^{i-1} \qquad \frac{dD_i}{dt} = \frac{1 - \alpha}{\alpha}k_p DL_i$$

Instantaneous growing probability functions

 $\boldsymbol{\alpha} = \frac{K_p M_s}{K_p M_s + K_t \mu_R^0 + E_r + \mu_E^0 + K_{fs} M_s + K_{fb} E_0}$

Primitive model construction (3) Hybrid methods for simulation (Cont.)

Step 2: Network fraction Original A Molecular weight distribution 0.6 Moles *n* 0.5 Chain Length LWeight fraction WfdWf/dLogM 0.4 0.3 0.2 0.1 2.5 3.5 4.5 5 5.5 6 6.5 3 4 Log (Molecular Weight) 1. Total activated units. N Moles 2. Soluble fraction for Chain Length I $Sf = \frac{C_{n \cdot N_A + N \cdot wf \cdot N_A - 2}^{n \cdot N_A + N \cdot wf \cdot N_A - 2}}{C_{n \cdot N_A + N \cdot wf \cdot N_A - 1}} \approx \frac{n}{n + N \cdot wf}$

Step 3: Combined distribution

1. Total Network

(A/A-g-B) network + Crosslinked B

- 2. Combined Molecular weight
 - A / B Non-Network

Grafting $P_g = \frac{n_{grafted-units}}{n_{total-units}}$

Combined Molecular Weight $L \cdot [M_A + P_g \cdot EX(M_{g-B})]$

Combined Mass

 $[W_A \cdot wf + n \cdot L \cdot P_g \cdot EX(M_{g-B})] \cdot Sf$

+ Homo-B

Primitive model construction (3) Hybrid methods for simulation (Cont.)



Model refinement and existing challenges Coefficients sub model

Update the parameter estimation with new experimental data for a good fit Simulation results





Model refinement and existing problems Model discrimination



Inversed problem for kinetic coefficients

Coefficients model discrimination

A lot of alternatives







- □ Whether the parameter is identifiable
- Define the evaluation criteria

Model refinement and existing problems Model discrimination (Cont)

Alternative models

- Polymer molecular theory
- Empirical formula
- Black-box model
- Discrimination Criteria
 - Physical acceptability
 - Compatibility with data diagnostic plot
 - Cp plot (Mallows,1964)
 - AIC score (Akaike, 1974)
 - The determinant of the parameter estimation equation (Bilardello, 1993)
 - Posterior probability (Stewart, etal. 1998)

Model refinement and existing problems Incremental Model Development

- □ More things are worth to be considered
- Multi-phase system
 - Phase behavior model
 - **D** Thermodynamic model for phase equilibrium
 - Molecular simulation (Coarse-grained model)
- Multi-Component Diffusion in polymeric liquids
 - Flux model
 - Macroscopic continuum thermodynamics and classical transport phenomena
 - Mesoscopic or coarse-grained level for complex fluids dynamics

Future work

- Develop a systematic model search approach for the model identification
- Goodness of fit test for the sub-model and structured model
- Model-based experimental design

Conclusion

- Kinetic model-based experimental design is one of the key technologies for chemical manufacturing process
- A primitive kinetic model is built for inter-polymer process
- Model refinement and discrimination is being developed with updating experimental data
- A systematic approach is needed for developing the integrated model structure