Modeling and optimization of Interpenetrating polymer network process

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Outline

- Introduction /overview
- Project progress and result discussion
- Proposals for future developments
- Summary

Interpenetrating polymer network (IPN)

- IPN – A combination of two polymers in a network form

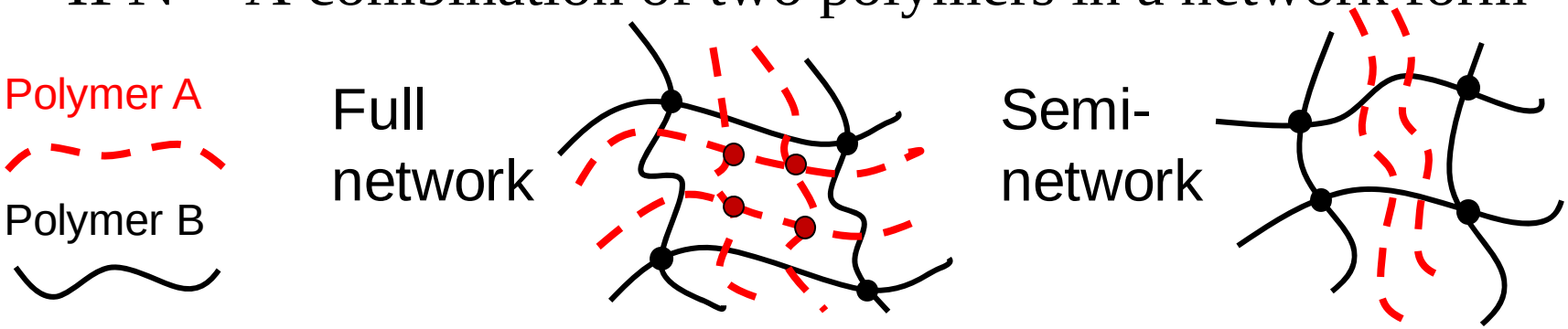


Fig. 1 IPN network structure

- An effective way to design new materials
  - Key characteristic : Tough & flexible
    - High value material

Huge market industry

Scaffold

Bone implant

Automotive parts

Complexity of IPN process

- Sequential process
  - sequentially build two polymer network by reaction control

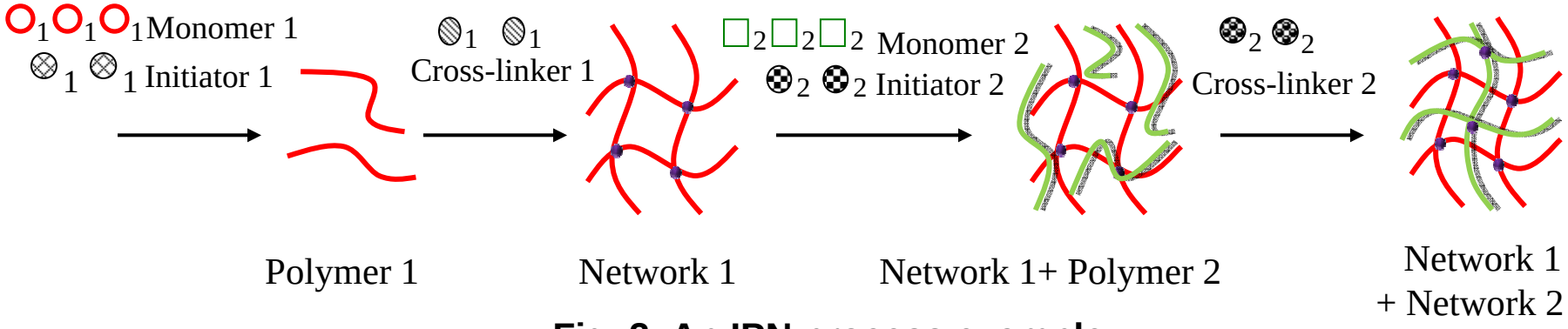


Fig. 2 An IPN process example

- Challenging to control and optimization
  - Difficult to predict final product properties under different process conditions due to complex polymer reaction and multi-component diffusion

Project overview

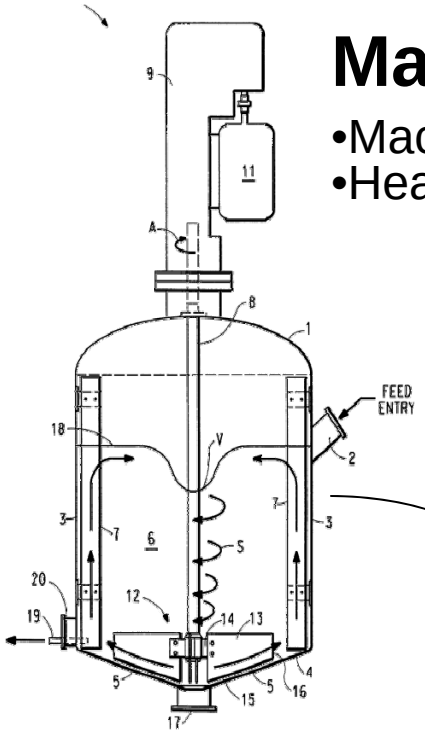
- **Goal:** construct a comprehensive model for IPN process development and quality control
- **Proposed plan**
  - No existing model available

    → Mechanism model construction
  - Missing chemical and physical parameters

    → Parameter estimation/ optimal experiment design
  - Various process alternative

    → Process optimization : Off-line/ On-line

Multi-scale modeling



Macro- Scale

- Macro-mixing
- Heat removal

Meso-Scale

- Mass transport
- Internal diffusion
- Particle morphology

Suspended particles

Micro-scale

- Formation of chains
- Intrinsic kinetics

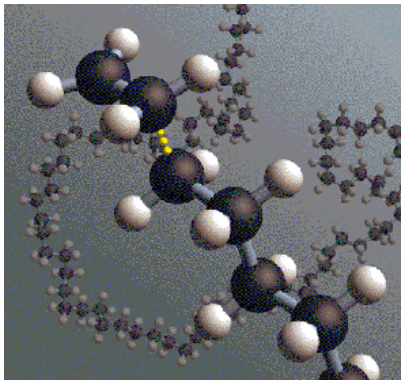


Fig. 3 Multi-scale model structure

Modeling development

- IPN kinetic model - **Reduce the complexity of chemical mechanism**
  - Polymer reaction – Active unit simplification
  - Combine molecular weight distribution - Finite moment method / Statistical assumption
- Single particle modeling - **Explore the process physics in particle scale**
  - Multi-component diffusion – Reaction diffusion model

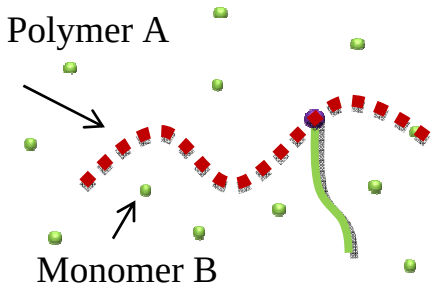
Level	Model	Model Outputs	Length Scale	Time Scale
Molecular level	Kinetic	Mn, Mw, MWD	angstrom	Sec
Single Particle	Reaction-diffusion	Particle growth rate, MWD, Concentration profiles Polymer microstructure	mm	Min

Micro-scale

IPN Kinetic model (1)

Reduce the complexity of chemical mechanism

Polymer Reactant



Network Product

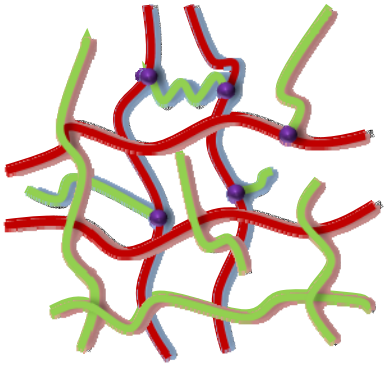


Table 1. A free radical polymerization example

Initiation reactions	Propagation reactions	Termination reactions	Transfer Reactions
$3M_s \xrightarrow{K_{in}} 2R_s^1$ $I_1 \xrightarrow{f_1 K_{d1}} 2R_{in_1}$ $I_2 \xrightarrow{f_2 K_{d2}} 2R_{in_2}$ $R_{in_1} + M_s \xrightarrow{K_i} R_s^1$ $R_{in_2} + M_s \xrightarrow{K_i'} R_s^1$ $R_{in_1} + E_0 \xrightarrow{K_2} E_R$ $R_{in_2} + E_0 \xrightarrow{K_2'} E_R$ $E_R + M_s \xrightarrow{K_3} E_{R_s}^1$	$R_s^i + M_s \xrightarrow{K_p} R_s^{i+1}$ $E_{R_s}^i + M_s \xrightarrow{K_p} E_{R_s}^{i+1}$	Homo-polymer $R_s^i + R_s^m \xrightarrow{K_t} P^{i+m}$ Grafting $R_s^i + E_R \xrightarrow{K_t} E_P^{i+m}$ $R_s^i + E_{R_s}^m \xrightarrow{K_t} E_P^{i+m}$ Cross-linking $E_R + E_R \xrightarrow{K_t} E_E$ $E_R + E_{R_s}^i \xrightarrow{K_t} E_{PE}$ $E_{R_s}^i + E_{R_s}^m \xrightarrow{K_t} E_{PE}^{i+m}$	$R_s^i + M_s \xrightarrow{K_{fs}} P^i + R_s^1$ $E_{R_s}^i + M_s \xrightarrow{K_{fs}} E_P^i + R_s^1$ $R_s^i + E_0 \xrightarrow{K_{fb}} P^i + E_R$ $E_{R_s}^i + E_0 \xrightarrow{K_{fb}} E_P^i + E_R$

Fig. 4 Active unit illustration

Micro-scale

IPN Kinetic model (2)

Average molecular weight – polymer moment model

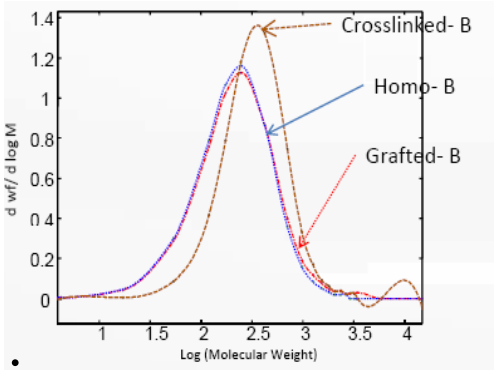
$$\overline{Mn} = \frac{(\mu_1 + \lambda_1)}{(\mu_0 + \lambda_0)} \times RM \qquad \overline{Mw} = \frac{(\mu_2 + \lambda_2)}{(\mu_1 + \lambda_1)} \times RM$$

Live moment $\mu^i = \sum_{n=1}^{\infty} n^i L_n$ Dead moment $\lambda^i = \sum_{n=1}^{\infty} n^i D_n$

Molecular weight distribution – Finite element method

$$f_{(m,n)} = \frac{\sum_{i=m}^{n} iD_i}{\sum_{i=2}^{\infty} iD_i} = \frac{weight\ of\ polymer\ with\ chain\ length\ from\ m\ to\ n}{total\ weight\ of\ polymer}$$

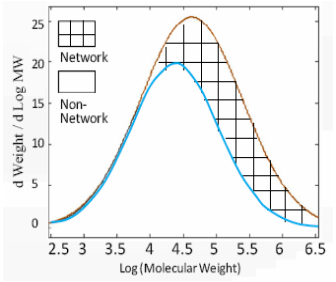
$$\frac{df_{(m,n)}}{dt} = \frac{1}{\lambda_1} \sum_{i=m}^{n} i \frac{dD_i}{dt} - \frac{f_{(m,n)}}{\lambda_1} \frac{d\lambda_1}{dt}$$

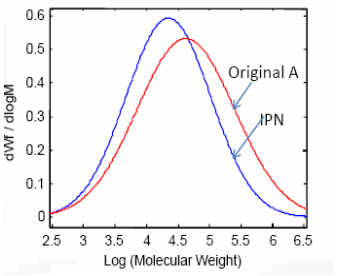


Semi-network structure – Statistic assumption

$$Sf = \frac{C^{n \cdot N_A - 2}_{n \cdot N_A + N \cdot wf \cdot N_A - 2}}{C^{n \cdot N_A - 1}_{n \cdot N_A + N \cdot wf \cdot N_A - 1}} \approx \frac{n}{n + N \cdot wf}$$

Fig. 5 Simulation examples





Meso-scale

Single particle modeling (1)

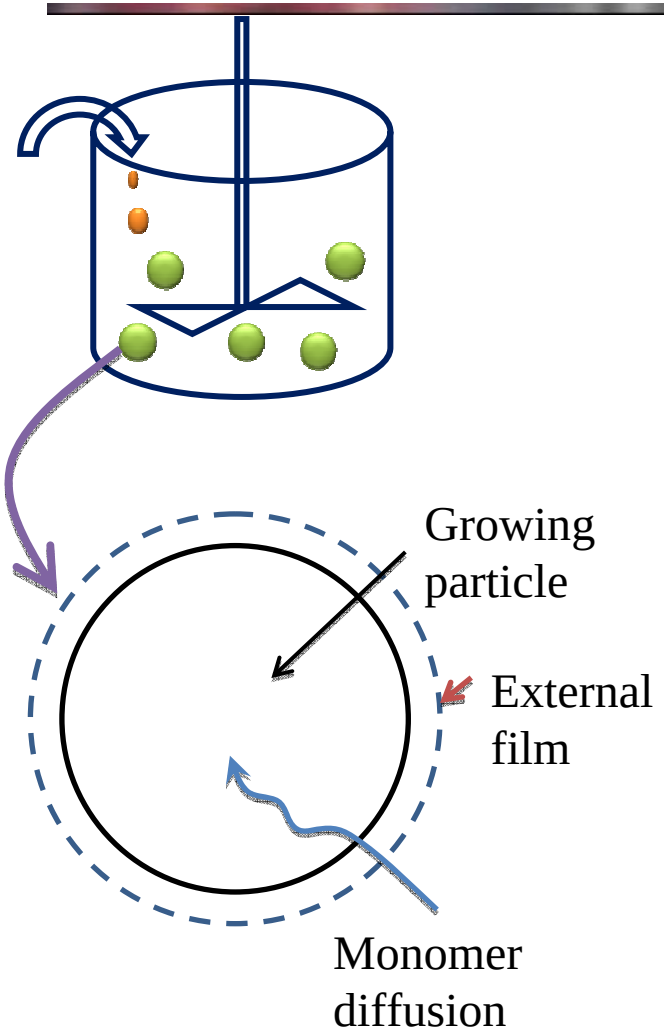


Fig. 6 Single particle model

Reaction-diffusion model

Unsteady-state mass balance conservation equation

$$C_i \nabla \cdot u + \frac{DC_i}{Dt} + \nabla \cdot j_i - r_i = 0$$

Fick's first law

$$j_i = -[D_{ij}] \nabla C_j$$

Intro-particle diffusion

u = 0

C_i Concentration
u Velocity
j_i Mass flux
r_i Consumption rate

Meso-scale

Single particle modeling (2)

Apply effective binary diffusion coefficient (EBDC)

$$j_i = -D^i_{eff}\nabla C_i, \quad (i = 1, 2, ...n) \qquad \frac{1}{D^i_{eff}} = \sum_{j=1, j\neq i}^{n} \frac{x_j}{D_{ij}}\left(1 - \frac{x_i N_j}{x_j N_i}\right)$$

Then mass balance equation becomes

$$\frac{\partial C_i}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D^i_{eff} r^2 \frac{\partial C_i}{\partial r}\right) - r_i$$

- Initial condition $C_i(r, t = 0) = C_{i0} \quad R_s(t = 0) = R_{s0}$
- Boundary condition

$$\frac{\partial C_i}{\partial t}|_{(r=0,t)} = 0$$

$$D_{eff_i}\frac{\partial C_i}{\partial r}(r = R_s(t), t) = k_s(C_{ie} - C_i)$$

Where r_i based on kinetic model, and R_s increase with time

Computational issues in modeling (1)

- Kinetic model – Stiff algebra-differential equation
  - Simulation – BDF method
  - Parameter estimation – Simultaneous approach

Dynamic optimization problem

$$Min \quad Tr(V^{-1}M(\theta)) = \sum_u \sum_j e_u^T V^{-1} e_u$$

$$\text{S.t.} \quad f(\frac{dx}{dt}, x, y, t) = 0$$

$$f(\frac{dx}{dt}|_{t=0}, x(0), y(0), 0) = 0,$$

$$x_L \le x \le x_U, y_L \le y \le y_U$$

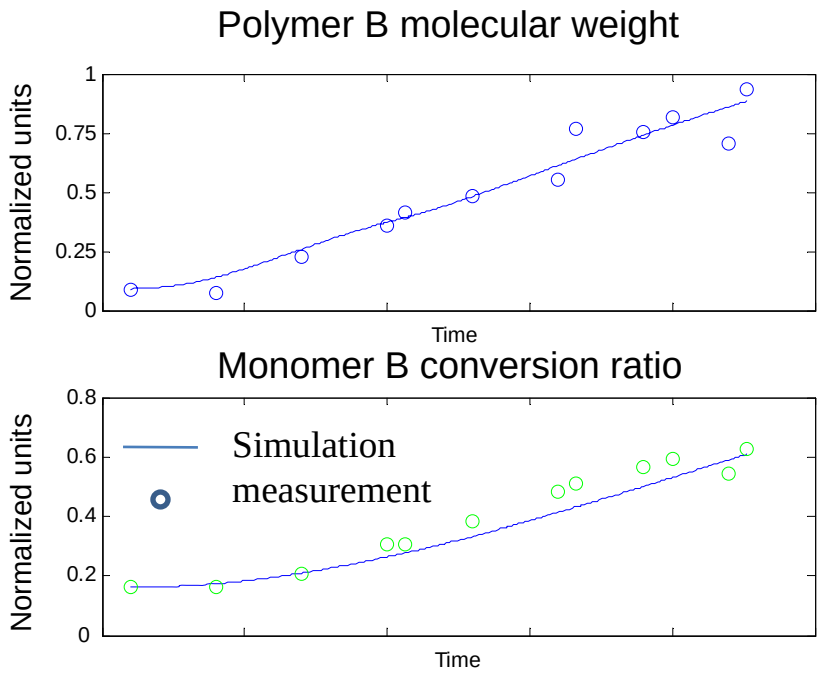


Fig. 7 Several fitting results

Computational issues in modeling (2)

- Reaction- diffusion model

Moving boundary partial differential equation with boundary integral condition

Simulation

- Boundary condition transformation

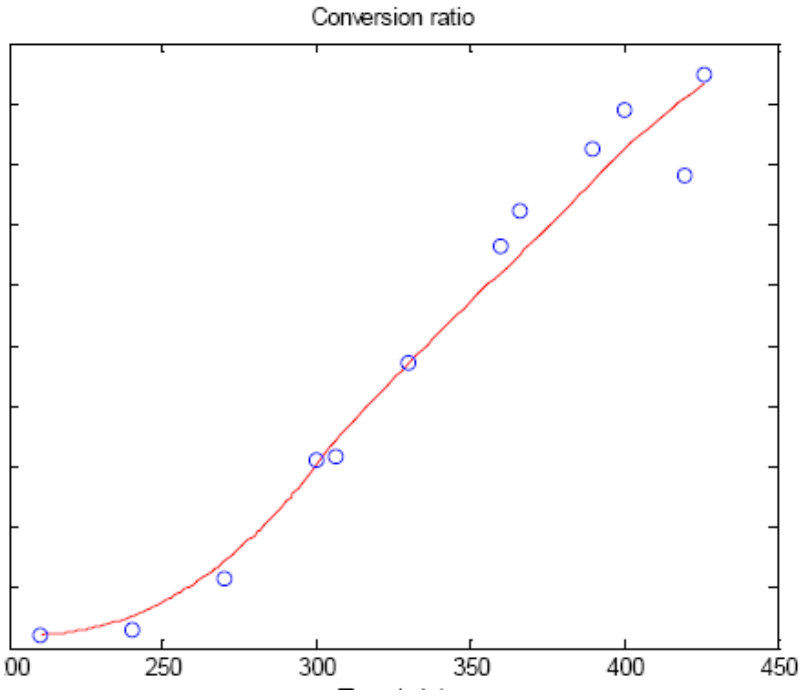
$$x(t) = \frac{r}{Rs(t)} \quad then \quad Y(r,t) \rightarrow Y(x(t),t)$$

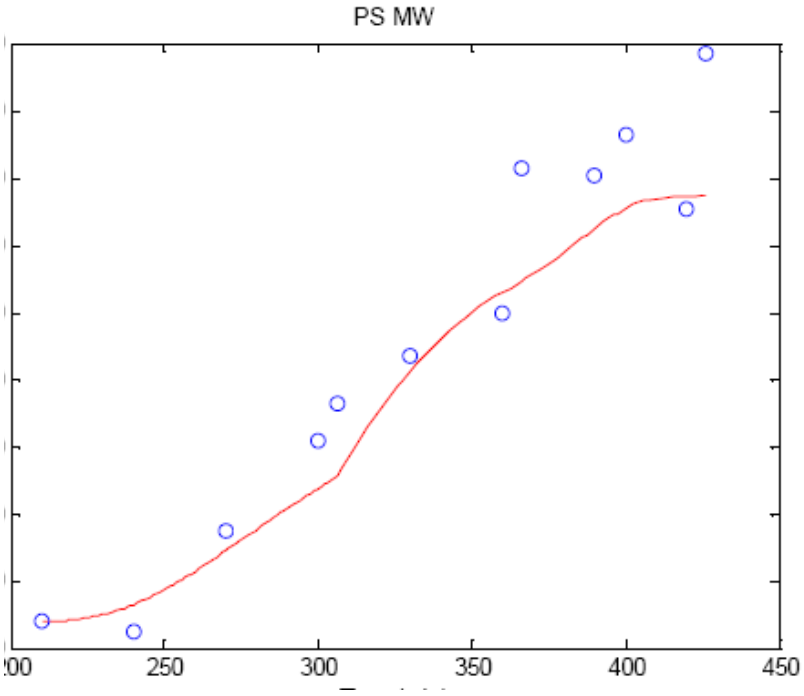
- Variable transformation

$$(\frac{\partial Y}{\partial r}) = (\frac{\partial Y}{\partial x} \cdot \frac{\partial x}{\partial r}) = \frac{1}{Rs} \cdot \frac{\partial Y}{\partial x}\,, \quad \frac{\partial^2 Y}{\partial r^2} = \frac{1}{Rs^2} \cdot \frac{\partial^2 Y}{\partial x^2}\,, \quad (\frac{\partial Y}{\partial t}) = \frac{\partial Y}{\partial t} - \frac{x \cdot \dot{Rs}}{Rs} \cdot \frac{\partial Y}{\partial x}$$

- Orthogonal collocation on finite elements
- Gaussian integral evaluation $\int_{-1}^{1} f(x)\,dx \approx \sum_{i=1}^{n} w_i f(x_i).$

Fitting with Diffusion Model





- Intermediate model results – Reaction Model
- Parameter estimation to MW and conversion data
- Minor refinements still needed in diffusion terms

Numerical issues in modeling (3)

- Some simulation results

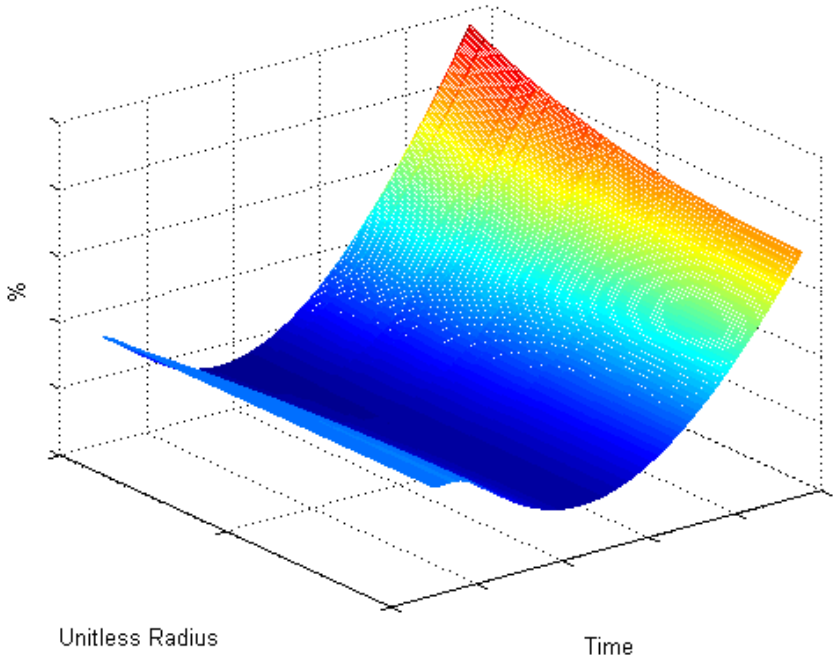


Fig. 8 Polymer B fraction inside the particle

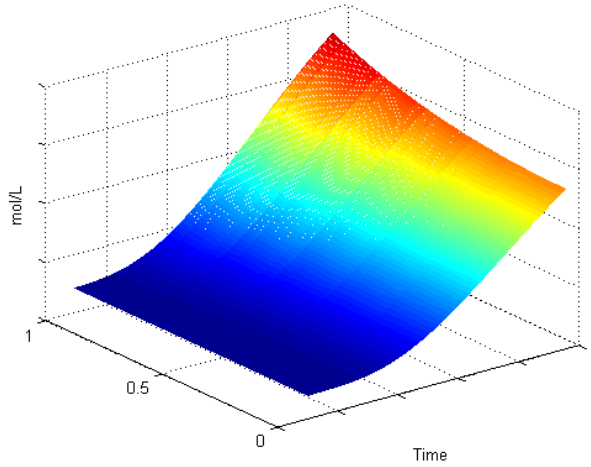


Fig. 9 Polymer B Mw

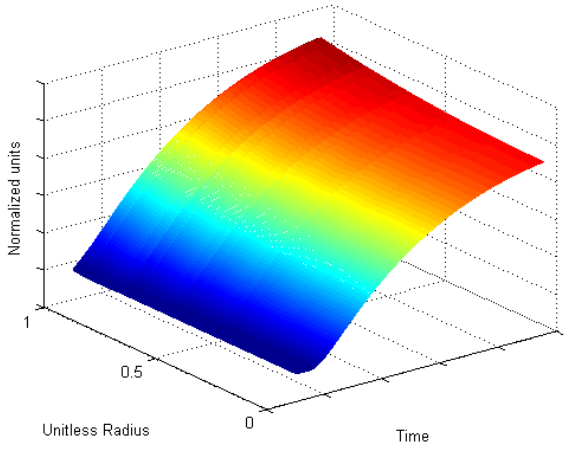


Fig. 10 Monomer concentration

Proposals for future development

- Parameter analysis
  - Simultaneous parameter estimation
  - Function modification
- Stage optimization – feeding policy related
  - Optimal boundary control problem
- Integrated model for production process
  - Build and connect model for different process stages
  - Larger scale optimization problem

Summary

- IPN is an advanced multi-polymeric material with versatile applications. An appropriate process models is crucial for its further development
- A preliminary multi-scale model is built for a semi-IPN process. Simulation and parameter estimation are being studied with current experimental data.
- Further parameter estimation technique and dynamic optimization problem are proposed for future investigation.