

Detailed Mathematical Modelling of the Emulsion Copolymerization of AN/Bd in Batch/Continuous & Trains of Continuous Reactors

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1. Introduction

COMMODITY rubbers, such as styrene-butadiene (SBR) or nitrile-butadiene (NBR) are industrially produced in large trains of continuous reactors using an emulsion polymerization process. Both SBR & NBR systems are largely unstudied. Furthermore, the studies that have been published on NBR have been typically limited to issues concerning the characteristics of the product behaviour.

The goal of this research is to develop a practical tool to predict polymer production rate and product quality (molecular weight averages and chain branching frequencies) on an industrial scale. Using the model predictions, properties of the resulting rubber can be estimated through correlating the model response to plant data. It is important to note the versatility of a model in this situation, as when given a set of desired product properties one could use the model to predict appropriate process operating conditions. Such a tool would considerably reduce product development time, as well as improve ones knowledge of the process.

2. Theory

IMPORTANT characteristics of the model are species partitioning among the different phases, particle nucleation via both micellar and homogeneous mechanisms, diffusion controlled kinetics, radical desorption, and the inclusion of both monomer and water soluble impurities.

The partitioning of monomer between the particle, droplet, and aqueous phases of an emulsion system is modelled using an empirical or thermodynamic approach. The empirical approach uses coefficients that represent the ratio of volume fractions of monomer in a particular phase. For example, a coefficient representing the fraction of monomer i in the droplet phase to the aqueous phase can be written as follows:

$$K_i^{d/a} = \frac{V_i^d/V_d}{V_i^a/V_a} = \frac{\phi_i^d}{\phi_i^a} \quad (1)$$

Using a similar equation for the aqueous and particle phases the concentration of monomer in each phase can be determined. For the particle phase the concentration can be stated as follows:

$$[M]_p = \frac{N_i}{K_i^{d/a} K_i^{a/p} V_d + K_i^{a/p} V_a + V_p} = \frac{\rho_i \phi_i^p}{MW_i} \quad (2)$$

The total particle surface area is given by:

$$A_p = (36\pi N_p)^{1/3} V_p^{2/3} \quad (3)$$

The total free micelle surface area available for micelle formation can be given as:

$$A_m = \sum_i^{N_{mic}} S_{a_i} ([E_i] - CMC) V_a N_A - A_p \quad (4)$$

A typical example of the model expressions for the rate of particle nucleation is as follows:

$$R_{hom} = k_h [R]_a^{hom} N_A \quad (5)$$

$$R_{mic} = R_{des}^{mic} + \frac{k_{cm} [R]_a^{mic}}{r_{mic}} N_A \quad (6)$$

$$[R]_a^{hom} = \sum_i [R]_{j,i} \frac{\mu H}{A_m + \varepsilon A_p + \mu H} \quad (7)$$

$$[R]_a^{mic} = \sum_i \sum_{k=\frac{j}{2}+1}^{j-1} [R]_{i,k} \frac{A_m}{A_m + \varepsilon A_p} + [R]_{j,i} \frac{A_m}{A_m + \varepsilon A_p + \mu H} \quad (8)$$

$$H = \begin{cases} \left(1 - \frac{LA_p}{4V_a}\right) V_a & \text{if } LA_p \leq 4V_a \\ 0 & \text{otherwise} \end{cases} \quad (9)$$

The polymerization kinetics are considered to fall between the case two and three regime, where the average number of radicals per particle will be around 0.5 at low conversions and increase as conversion increases. A common approach for determining \bar{n} is that proposed by Ugelstad et al in the form of a recursive equation seen below:

$$\bar{n} = \frac{\alpha}{p + 1 + \frac{2\alpha}{p + 2 + \dots}} \quad (10)$$

3. Model Formulation

THE model is cast in a dynamic form using ordinary differential equations to describe the mass, particle, and moment balances.

$$\frac{dN_j}{dt} = F_{j,in} - F_j - \sum_k R_{j,k} V_k \quad (11)$$

$$\frac{dN_p}{dt} = F_{p,in} - F_p + (R_{mic} + R_{hom}) V_a \quad (12)$$

$$\frac{dV_p}{dt} = q_{p,in} - q_p + growth \quad (13)$$

$$growth = \begin{cases} \sum_i^N \frac{MW_{m_i} (R_{p_{m_i}} V_a + R_{p_{p_i}} V_p)}{\phi_{p_i}} & \text{if } V_d > 0 \\ \sum_i^N \frac{MW_{m_i} R_{p_{m_i}} V_a + \sum_j^N MW_{m_j} R_{p_{m_j}} V_p \left(\frac{1}{r_{m_i}} - \frac{1}{r_{p_i}}\right)}{\phi_{p_i}} & \text{otherwise} \end{cases}$$

$$\frac{d(V_p Q_i)}{dt} = (q_p Q_i)_{in} - (q_p Q_i) + R_Q V_p \quad (14)$$

Due to the scale of the different states (e.g. particles, moles, volume), the system is quite stiff. Thus, an appropriate integration solver (CVODE) must be used to handle the system stiffness.

4. Simulation Results

THE following figures show typical model simulations for batch and continuous reactors. CSTR simulations were performed using a residence time of 60 minutes per reactor and a start up procedure full of water with all ingredients fed to the first reactor.

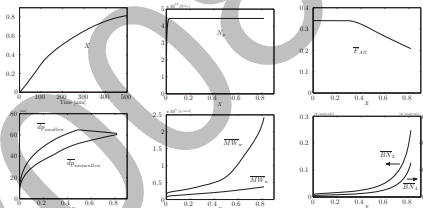


Figure 1: Batch simulation, (a) conversion, (b) number of particles, (c) cumulative copolymer composition, (d) average particle diameter: swollen (polymer + monomer) & unswollen (polymer), (e) molecular weights, (f) branching frequencies

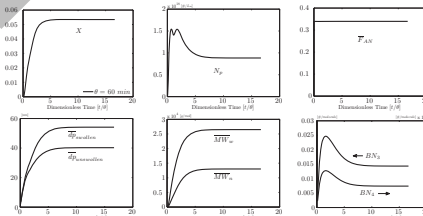


Figure 2: CSTR simulation, (a) conversion, (b) number of particles, (c) cumulative copolymer composition, (d) average particle diameter: swollen (polymer + monomer) & unswollen (polymer), (e) molecular weights, (f) branching frequencies

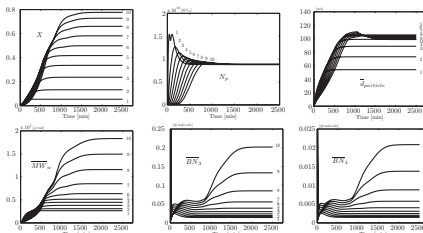


Figure 3: Dynamic CSTR Train simulation, (a) conversion, (b) number of particles, (c) average particle diameter: swollen (polymer + monomer), (d) weight average molecular weight, (e) tri- & (f) tetra-branching frequencies

5. Discussion

FROM an industrial perspective, conversion, copolymer composition, particle number & size, molecular weight and branching characteristics are all very important process/product indicators. Of all possible model predictions, molecular weights and branching frequencies are of considerable importance due to their direct influence on polymer quality and processability. From the figures it is evident that without the addition of CTA the molecular weight and degree of branching increase sharply beyond 60 % conversion. Thus, in order to maintain the molecule weight in a desired range as well as to minimize the chain branching, optimal control policies are needed for the addition of CTA along the reactor train. Also apparent is the need to control the composition of AN in the copolymer. This can be accomplished through the addition of AN in down stream reactors.

Though no literature data is available for an NBR system, the model has been found to be in good agreement with literature data for the batch emulsion homopolymerization of Bd.

6. Concluding Remarks

MODELS that capture the detailed mechanism and dynamics of the polymerization process can be tremendously useful in an industrial environment. For example, developing reactor startup procedures, monitoring transient effects when changing the polymer grade or when switching a reactor in or out of the train, developing on-line control strategies, and developing soft sensors for monitoring various polymerization properties on-line. The work presented here is the beginning of an extensive study to develop a practical tool for monitoring, controlling and optimizing the process behaviour on-line during the production of NBR in a continuous reactor train.

As industry strives to deliver more customer specific products, it will be the underlying models, which aid in controlling the process, that govern how well industry targets meet customer requirements. Thus, an accurate and robust model is key before developing optimal operating and control policies.

7. Nomenclature

A_m, A_p	Free micellar area & surface area of particles
$[E_i], CMC$	Concentration of emulsifier & critical micelle concentration
F_j, F	Molar flow of species j in/out of the reactor
E_j	Homogeneous nucleation grouping term
$K_i^{d/a}$	Partition coefficient for monomer i between phases d & a
N_j, N_p	Total number of moles of species j & number of particles
\bar{n}	Average number of radicals per particle
q_{in}, q_i	Volumetric flow rate of phase k in/out of the reactor
Q_i	i^{th} moment of the molecular weight distribution
$[R]_a$	Concentration of radicals of length k ending in monomer i
$[R]_a^{mic}, [R]_a^{hom}$	Concentration of radicals capable of being captured by micelles & particles
$k_{p_i}, R_{p_i}^{mic}$	Rate of polymerization of monomer i in phase k & rate of radical capture
V_a, V_p, ϕ_i^k	Volume of phase k & Volume and volume fraction of monomer i in phase k
ε, μ	$(k_{d_i}/k_{tm}), (k_{d_i}/k_{tm})$
α, p	Dimensionless grouping terms