# Modeling the Transient Behavior of Continuous Emulsion Polymer Reactors

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Kiparissides et al. (1978) developed a system of model equations, the solution of which was used to simulate transient continuous emulsion polymer data reported by Greene et al. (1976). Their comprehensive model agreed quite well with the data obtained for the continuous emulsion polymerization of vinyl acetate. Their model, however, involved the solution of integrodifferential equations. The objective of this study is to show that the model equations developed by Kiparissides et al. (1978) can be transformed to purely differential form, the solutions of which are easier to obtain and should be more accurate than the solution of integrodifferential equations. Even though the nonlinear differential equations are stiff, the predictor-corrector method used to integrate them gives solutions in reasonable amounts of computer time. Some results are shown for comparison.

We will not reproduce the details of the development of the model because it is available in the article by Kiparissides et al. (1978). To simplify matters, we use the same nomenclature they used. When referring to their equations, we prefix their number with *H*.

The average number of radicals in a polymer particle was given by

$$\overline{q}(t,\tau) = \left( \frac{R_I(t)}{2k_{de}(t,\tau)n(t,\tau)d\tau} \right)^{1/2} \left( \frac{A_n(t,\tau)d\tau}{A_p(t)} \right)^{1/2} \qquad (H\text{-}16)$$

where the free radical desorption coefficient was

$$k_{de}(t,\tau) = \frac{12D_w\delta}{m(t)D_p^2(t,\tau)} \left( \frac{k_{fm}}{k_p} \right) \qquad (H\text{-}17)$$

The surface area of the $n(t,\tau)d\tau$ class particles is given by

$$A_n(t,\tau)d\tau = a_p(t,\tau)n(t,\tau)d\tau \qquad (1)$$

When equations (*H*-17) and (1) are combined with (*H*-16), we have

$$\overline{q}(t,\tau) = \left( \frac{k_pR_I(t)m(t)}{24\pi D_w\delta k_{fm}} \right)^{1/2} \left( \frac{a_p^2(t,\tau)}{A_p(t)} \right)^{1/2} \qquad (2)$$

where we have used

$$a_p(t,\tau) = \pi D_p^2(t,\tau) \qquad (3)$$

$R_I(t)$ and $m(t)$ are time dependent functions given by

$$R_I(t) = 2fk_d[I]_{\text{feed}}(1 - e^{-t/\theta}) \qquad (4)$$

and

$$m = m_0(1 - e^{-t/\theta}) \qquad (H\text{-}20)$$

for the start-up conditions used by Greene et al. (1976).

The volumetric growth rate of particles is related to the reactor environment by

$$\frac{\partial v_p(t,\tau)}{\partial t} = \frac{k_pd_m\phi(t)}{N_ad_p(1-\phi(t))}\overline{q}(t,\tau) \qquad (H\text{-}11)$$

which, when combined with Equations (2), (4), and (*H*-20), becomes

$$\frac{\partial v_p(t,\tau)}{\partial t} = \frac{k_pd_m\phi(t)}{N_ad_p[1-\phi(t)]} \left[ \frac{k_pfk_d(I)_{\text{feed}}m_0}{12\pi D_w\delta k_{fm}} \right]^{1/2} (1 - e^{-t/\theta}) \frac{a_p(t,\tau)}{A_p^{1/2}(t)} \qquad (5)$$

Equation (5) may be collected into three parts as

$$\frac{\partial v_p(t,\tau)}{\partial t} = \lambda \cdot \zeta(t) \cdot a_p(t,\tau) \qquad (6)$$

only one part of which depends on the nucleation time $\tau$.

The particle nucleation function describing both micelle and homogeneous phase particle generation is

$$f(t) = \rho(t) \left\{ \frac{k_vA_m(t) + \mu[1 - LA_p(t)/4]}{k_vA_m(t) + k_v\epsilon A_p(t) + \mu[1 - LA_p(t)/4]} \right\} \qquad (H\text{-}28)$$

where

$$k_v = V_p(t)/[1 - V_p(t)] \qquad (7)$$

and

$$A_m(t) = [S_F(1 - e^{-t/\theta}) - S_{cmc}]s_\alpha - A_p(t) \qquad (H\text{-}24)$$

The free radical production rate $\rho(t)$ is comprised of contributions from initiator decomposition and radical desorption from particles:

$$\rho(t) = R_I(t) + \int_0^t k_{de}(t,\tau)n(t,\tau)\overline{q}(t,\tau)d\tau \qquad (8)$$

The integrand in Equation (8) can be shown, using Equations (*H*-16), (*H*-17), and (1), to be

$$\left[ \frac{R_I(t)}{A_p(t)m(t)} \right]^{1/2} \left( \frac{6\pi D_w\delta k_{fm}}{k_p} \right)^{1/2} n(t,\tau) \qquad (9)$$

The integration in Equation (8) is with respect to the nucleation time $\tau$, and all time dependent quantities are independent of $\tau$. Thus, Equation (8) may be reduced to

$$\rho(t) = 2fk_d[I]_{\text{feed}}(1 - e^{-t/\theta}) + \left[ \frac{12\pi D_w\delta k_{fm}(I)_{\text{feed}}}{m_0k_p} \right]^{1/2} \frac{N(t)}{A_p^{1/2}(t)} \qquad (10)$$

Now that $\rho(t)$, the radical generation rate, is known, everything is known about the particle nucleation function $f(t)$ in Equation (*H*-28).

We now develop the set of differential equations which must be solved to completely describe the continuous emulsion polymer system. The transient balance on total particles is given by

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$$\frac{dN(t)}{dt} = -\frac{N(t)}{\theta} + f(t) \qquad (H\text{-}29)$$

The time derivative of the cumulative particle diameter function is found as follows:

$$\frac{dD(t)}{dt} = \frac{d}{dt}\int_o^t D_p(t,\tau)n(t,\tau)d\tau$$
$$= \frac{d}{dt}\int_o^t D_p(t,\tau)f(\tau)e^{-(t-\tau/\theta)}d\tau$$
$$= \int_o^t \frac{\partial D_p(t,\tau)}{\partial t dt}\cdot f(\tau)e^{-(t-\tau/\theta)}d\tau$$
$$-\frac{1}{\theta}\int_o^t D_p(t,\tau)f(\tau)e^{-(t-\tau/\theta)}d\tau + D_p(t,t)f(t) \qquad (11)$$

where Liebnitz's rule and the chain rule have been used simultaneously to arrive at Equation (11). The following expression was used to relate the number of particles to their age:

$$n(t,\tau)d\tau = f(t)e^{-(t-\tau/\theta)}d\tau \qquad (H\text{-}3)$$

The time derivative of $D_p(t, \tau)$ is found by simply changing Equation (6) from a volume to a diameter basis. Simplification of the terms in Equation (11) results in the balance for $D(t)$:

$$\frac{dD(t)}{dt} = 2\lambda\zeta(t)N(t) - \frac{D(t)}{\theta} + D_p(t,t)f(t) \qquad (12)$$

Similar treatment of the time derivative of $A_p(t)$ and $V_p(t)$ results in

$$\frac{dA_p(t)}{dt} = 4\pi\lambda\zeta(t)D(t) - \frac{A_p(t)}{\theta} + a_p(t,t)f(t) \qquad (13)$$

and

$$\frac{dV_p(t)}{dt} = \lambda\zeta(t)A_p(t) - \frac{V_p(t)}{\theta} + v_p(t,t)f(t) \qquad (14)$$

The rate of polymerization is given by

$$R(t) = \int_o^t \frac{k_p d_m \phi(t)}{N_a M_w}\bar{q}(t,\tau)d\tau$$

or

$$= \frac{1-\phi(t)}{M_w} d_p\lambda\zeta(t)A_p(t) \qquad (15)$$

The equation for monomer conversion is developed from the material balance for monomer:

$$\frac{dM(t)}{dt} = \frac{M_F - M(t)}{\theta} - R(t)$$

Using

$$X(t) = 1 - \frac{M(t)}{M_F(1-e^{-t/\theta})}$$

one has

$$\frac{dX(t)}{dt} = (1-e^{-t/\theta})^{-1}\left\{\frac{R(t)}{M_F} - \frac{X(t)}{\theta}\right\} \qquad (16)$$

The definition for conversion accounts for the increasing amount of organic material in the reactor during start-up of the system.

Equations ($H$-29) and (12) to (16) form a closed set of nonlinear first-order differential equations, the solution of which provides values for the dependent variables $N(t)$, $D(t)$, $A_p(t)$, $V_p(t)$, $R(t)$, and $X(t)$. The time dependent functions $f(t)$ and $\zeta(t)$ are given in this work. The quantities $D_p(t, t)$, $a_p(t, t)$, and $v_p(t, t)$ should be evaluated at micelle size. The function $\phi(t)$ is a constant if monomer droplets exist and is given by

$$\phi(t) = \frac{1-X(t)}{1-X(t)(1-d_m/d_p)} \qquad (H\text{-}1)$$

if monomer droplets do not exist.

The differential equations just developed were solved numerically on the DEC-10 computer at WACCC using a standard predictor-corrector technique with adjustable time increment. Green's start-up procedure of having degassed water in the reactor initially was used as the starting point for the computer simulation.

Figure 1 shows the comparison of Green's experimental data to both Hamielec's comprehensive simulation and our numerical integration. The numerical values of the constants used in our calculations are shown in Table 1. The results from our simulation required just over 2 min of CPU time. In addition to the transient conversion trajectory shown, the computer printed the time dependent values of $N(t)$, $D(t)$, $A_p(t)$, $V_p(t)$, and $R(t)$. We neglected to show these quantities for brevity.

The careful reader will note several features in these results. First, our simulation of the experimental data is not as good as one might hope. Presuming the experimental data were carefully collected and accurately reported, one must conclude the model is not adequate, or the values of the constants used were not appropriate for the experimental system. The model is almost the same one developed and solved by Kiparissides et al. (1978); thus the values of the constants used should be questioned.

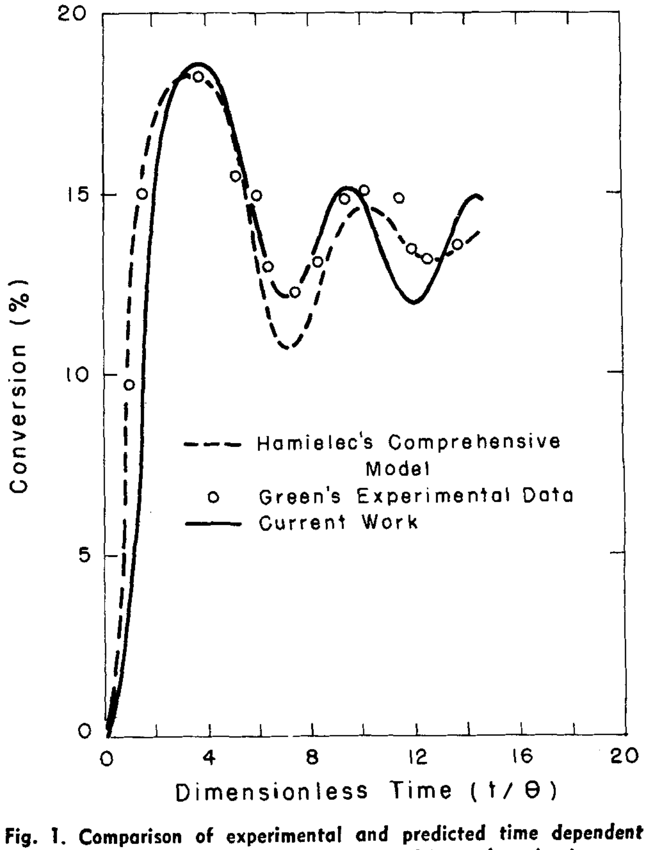

**Fig. 1. Comparison of experimental and predicted time dependent conversion values for vinyl acetate emulsion polymerization.**

TABLE 1. NUMERICAL VALUES OF THE CONSTANTS USED

$D_w$ = $10^{-7}$ dm²/s
$d_m$ = 930 g/l
$d_p$ = 1 150 g/l
$D_p(t, t)$ = 54A
$fk_d$ = $2.5 \times 10^{-7}$ s$^{-1}$
$(I)_{\text{feed}}$ = 0.01 mole/l
$k_{fm}$ = 0.75 l/mole · s
$k_p$ = 4 068 l/mole · s
$L$ = $1.29 \times 10^{-4}$ dm
$M_F$ = 3.42 mole/l
$m_0$ = $M_F/M_{\text{water}} = 10.36$
$S_{cmc}$ = $4.0 \times 10^{-3}$ mole/l
$S_F$ = 0.01 mole/l
$s_\alpha$ = $6.10 \times 10^{-17}$ dm²/molecule
$\delta$ = 0.55
$\epsilon$ = 5.0
$\mu$ = 1.6 dm$^{-1}$
$\phi_{\text{sat}}$ = 0.813

There are, in fact, no less than twelve independent parameters associated with this model. We used different values for some parameters than did Kiparissides et al. When we used their values, the simulation results did not coincide with the experimental data.

Simulation results were compiled using various parameter values until a reasonable fit to the existing data was achieved. We note that the values of fully half of the independent parameters are uncertain, these being the ones we varied to obtain the current results. We feel certain that at least one combination of parameter values would force the theoretical predictions through all the data points, but we question the merit of the exercise until values of some constants are known from independent experiments.

Several trends in the behavior of the simulation were noted:

1. Increasing the micelle size $D_p(t, t)$ increased the frequency of oscillations but decreased their amplitude.
2. Increasing the growth rate parameter $k_p$ increased the frequency slightly but increased the amplitude appreciably.
3. An increase in $\epsilon$ increased the amplitude of the oscillations when micelle nucleation occurred.
4. An increase in $\delta$ increased both the amplitude and the period of oscillation.
5. The presence of soap and monomer in the reactor initially resulted in a higher initial peak due to the occurrence of micelle nucleation.
6. The standard deviation of the particle size distribution is predicted to be constant during periods when nucleation does not occur.

We have demonstrated that the integrodifferential model presented by Kiparissides et al. (1978) can be transformed to a purely differential form. The model equations were easily solved by conventional methods, and the results are shown to agree reasonably well with data from the literature. The experience we have had with the simulation thus far suggests the system is quite sensitive to variations in parameter values. The predictive utility of this model will be much greater when values of the constants are known for various emulsion polymer systems.

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## NOTATION

$A_m(t)$ = total micelle surface area
$A_n(t, \tau)d\tau$ = total surface area of $n(t, \tau)d\tau$ type of particle
$A_p(t)$ = total polymer particle surface area
$a_p(t, \tau)$ = surface area of an $n(t, \tau)d\tau$ type of particle
$D(t)$ = total polymer particle diameter
$D_p(t)$ = diameter of an $n(t, \tau)d\tau$ type of particle
$D_w$ = diffusion coefficient of monomeric radicals in water
$d_m$ = monomer density
$d_p$ = polymer density
$f$ = initiator decomposition efficiency
$fk_d$ = effective initiator decomposition rate constant
$f(t)$ = particle nucleation rate
$(I)_{\text{feed}}$ = initiator concentration in the feed
$k_{de}(t, \tau)$ = free radical desorption rate constant
$k_{fm}$ = rate constant for chain transfer to monomer
$k_p$ = polymerization rate constant
$k_v$ = volume ratio of polymer to aqueous phase
$L$ = critical diffusion length
$M_F$, $M(t)$ = feed and effluent monomer concentrations
$M_w$ = molecular weight of monomer
$m(t)$ = monomeric radical partition coefficient between water and particle phases
$N_a$ = Avogadro's number
$N(t)$ = total number of particles
$n(t, \tau)d\tau$ = number of particles at time $t$ born within time internal $\tau$ to $\tau + d\tau$
$\bar{q}(t, \tau)$ = average number of radicals per particle for $n(t, \tau)\, d\tau$ type of particles
$R(t)$ = polymerization rate
$R_I(t)$ = radical initiation rate
$S_F$ = emulsifier concentration in feed
$S_{cmc}$ = critical micelle concentration
$s_\alpha$ = area covered by one molecule of emulsifier
$t$ = time
$V_p(t)$ = total polymer particle volume
$v_p(t, \tau)$ = volume of an $n(t, \tau)d\tau$ type of particle
$X(t)$ = monomer conversion

### Greek Letters

$\delta$ = lumped monomeric radical diffusion coefficient
$\epsilon$ = ratio of radical absorption rate to micelle nucleation rate
$\zeta(t)$ = time dependent function = $(1 - e^{-t/\theta})\,\phi(t)/1 - \phi(t)\, A_p^{-1/2}(t)$
$\rho(t)$ = free radical initiation rate
$\theta$ = average residence time
$\lambda$ = constant $= \dfrac{k_p d_m}{N_a d_p}\left(\dfrac{k_p f k_d [I]_{\text{feed}} m_0}{12\pi D_w \delta k_{fm}}\right)^{1/2}$
$\tau$ = nucleation time
$\phi(t)$ = monomer volume fraction in particles
$\phi_{\text{sat}}$ = saturation value of monomer volume fraction in particles

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