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A Model to Study the Effect of Monomer Flow Rate on Methyl Methacrylate Emulsion Polymerization in a Seeded Semi-Batch Reactor

Swati Gangwar¹, Ashwini Sood²

¹M. Tech. Student, ²Associate Professor, Department of Chemical Engineering, Harcourt Butler Technical University, Kanpur-208002, INDIA

Abstract: A mathematical model is developed, solved and validated to describe seeded semi-batch emulsion polymerization of the methyl methacrylate in the presence of sodium laurylsulfate as an emulsifier and potassium persulfate as an initiator. The assumption of monodispersed particle size distribution (all the particles have the same size at the given time) is used in developing the model. In the seeded semi-batch reactor, some amount of monomer is present initially in the reactor along with an emulsifier, initiator and water. After a certain pre-feed time or after the seeding stage, rest amount of monomer is fed in the reactor till it is completely fed. This is called feeding stage. After the feeding stage, the monomer inside the reactor reacts to completion; all the monomer is converted to polymer. The effect of two different monomer feed rates on the variation of conversion with time at 50 °C isothermal reactor operation, keeping all the other ingredients constant are studied by the model. The parameters of the model are obtained from literature and it is observed that incorporation of free radicals exit from the particles in an aqueous phase radical balance leads to a close agreement between model predictions and experimental data for the variation of conversion with time.

Keywords: Computer model, emulsion polymerization, methyl methacrylate, semi-batch reactor.

I. INTRODUCTION

Emulsion polymerization is a kind of the radical polymerization which generally begins with the emulsion having water, monomer, and surfactant. Emulsion polymerization has been utilized in the batch, semi-batch, and continuous processes. The selection is based on the characteristics of the final polymer or economics of the product. Semi-batch emulsion polymerization method is used to develop various types of latex. Latexes are generally not utilized in their pure form, but are compounded to changeable degrees with other components to tailor them to their intended applications. Pigments and thickeners are added in the latexes to improve their optical and rheological characteristics. Emulsion polymerization is preferred over other polymerization techniques especially because of high molecular weight of polymers obtained, the low viscosity of the latex, to increase the safety and productivity of the reaction, and for being friendlier to the environment. The ingredients of semi-batch generally contain a feed of monomer or emulsified monomer to the reactor. The semi-batch reactor is used because it has various advantages such as easily temperature control, easily removal of the enormous heat generated during the reaction and less amount of coagulum.

In this work, we have selected to study the emulsion polymerization of methyl methacrylate to poly methyl methacrylate (PMMA) in the presence of potassium persulfate (initiator), sodium dodecyl sulfate (emulsifier) with water as the dispersion medium in a seeded semi-batch reactor. Poly methyl methacrylate is an important polymer with several commercial uses. PMMA is also called acrylic or acrylic glass as well as by the trade names Plexiglas, Acrylite, Lucite and Perspex among numerous others, is a clear thermoplastic utilized in a sheet form as a lightweight, shatter-resistant choice to glass or in pellet form. The same material can be utilized as the casting resin, in the ink and coating and has various other uses.

II. OVERALL REACTOR BALANCES

Overall reactor balances (equations (1) – (6)) contain the material balances for monomer [M], polymer [P] and initiator [I], balance of the volume of reaction mixture (V_R) and the number of particles produced (N_p). The material balance, which defines the rate of change of moles of each species in the reactor, contains input, accumulation and reaction terms. The volume of the reaction mixture varies due to the monomer feed and difference in densities of monomer and polymer produced. The monomer inflow terms (Q_M) will have non-zero values during the monomer feeding time and will be zero during the pre-feed time and also when all the monomer is fed to the semi-batch reactor.

$$\frac{d[M]_R V_R}{dt} = Q_M [M]_f - R_p V_R \quad (1)$$

$$\frac{d[P]_r V_r}{dt} = R_p V_r \quad (2)$$

Where Rate of polymerization = R_p

$$R_p = \frac{k_p \rho_M}{M W_M} N_p \phi i \quad (3)$$

$$\frac{d[I] V_w}{dt} = -k_d [I] V_w \quad (4)$$

$$\frac{d[V]_R}{dt} = Q_M - \left(\frac{1}{\rho_M} - \frac{1}{\rho_P} \right) R_p M W_M V_R \quad (5)$$

$$\frac{dN_p}{dt} = R_n = k_{mm} A_m [R] \quad (6)$$

The rate of micellar nucleation (R_{em}) will be defined by radical entry rate into micelles. The entry of radical into micelles (and particles) has been assumed to take place via various mechanisms; the two significant ones being entry of the radical due to diffusion and entry of the radical due to collision. In this work the rate of radical entry micelles (R_{em}) is defined by:

$$R_{em} = k_{mm} A_m [R] \quad (7)$$

The rate of radical entry is coupled to an aqueous phase radical, which is provided by equation (8), which employs the quasi-steady state balance for an aqueous phase radicals. This equation merges the radical formation rate by decomposition of initiator in an aqueous phase, termination in an aqueous phase, entry of the radical into particles, entry of the radical into micelles, and radical exit from the particles.

$$2fk_d[I] - k_{tw}[R]^2 - k_{mp}A_p[R] - k_{mm}A_m[R] + k_{des}N_p i = 0 \quad (8)$$

By ignoring the aqueous phase termination and radical exit, and resolving the following equation for $[R]$, one gets equations.

$$[R] = \frac{2fk_d[I]}{k_{mm}A_m + k_{mp}} \quad (RAD1)$$

It has been suggested that exit radicals would not come in micelles although might re-enter in polymer particles. In order to analysis this we also assumed the following radical balance where the radicals exit from the particles was also taken in radical balance so;

$$2fk_d[I] - k_{mp}A_p[R] - k_{mm}A_m[R] + k_{des}N_p i = 0 \quad (9)$$

$$[R] = \frac{2fk_d[I] + k_{des}N_p i}{k_{mm}A_m + k_{mp}A_p} \quad (RAD2)$$

A. Particle Growth

The growth rate of particle rate (R_g) is defined by the equation (10) that shows the rate of reaction (in gm (polymer) sec) in the particles including average number of radical per particles and monomer volume fraction ϕ ;

$$R_g = \frac{dm_p}{dt} = \frac{k_p i \phi d_m}{N_A} \quad (10)$$

The volume of monomer- swollen latex particle (v) may be correlated to the mass of polymer (m_p) it contains:

$$v = \frac{m_p}{d_p(1-\phi)} \quad (11) \text{ To solve the two equations, which together provide the volume of the latex particle}$$

at any time, include two variables; monomer volume fraction within the particles (ϕ) and the number of radicals within the particles (i) the evaluation of these variables is given in the following sections.

B. Monomer Volume Fraction in the Particles

The diffusion of monomer into the polymer particles normally takes places at a fast rate. Therefore it can almost be assumed that the concentration of the monomer within the particle is at its equilibrium value at all times. The equilibrium concentration of the monomer can be found form the following correlation which is given by Min and Ray [1, 2], which is an expansion of that formed by Morton et al.[3].

$$\frac{2\gamma M W_M}{r \rho_M R_G T} + (1-\phi + \ln \phi - \chi (1-\phi)^2) = \ln \frac{[M]_w}{[M]_{SAT}} \quad (12)$$

Where γ is the interfacial tension, $M W_M$ is the molecular weight of the monomer, R is the universal gas constant, T is the absolute temperature, $[M]_w$ is the concentration of monomer in an aqueous phase. $[M]_{SAT}$ is the concentration of monomer at saturation in an aqueous phase, χ is the flory-Huggins interaction parameter and r is the radius of swollen particle. The radius of particles can be defined as;

$$r = r_{dry} / (1-\phi)^{1/3} \quad \text{Where, } r_{dry} = [3/4\pi (N_{m0} * X * \frac{M W_M}{\rho_P * N_P})]^{1/3}$$

C. Average Number of Radicals per Particle

The average number of radicals per particle is defined by the radical entry rate into, exist from and termination within particles. This is provided by the equation (13) that is the Smith–Ewart [4] recursion relation.

$$k_e[F_{i-1}(v,t)-F_i(v,t)+k_{des}[(i+1)F_{i+1}(v,t)-iF_i(v,t)] + (k_{tp}/2VN_A) [(i+2)(i+1)F_{i+2}(v,t)-i(i-1)F_i(v,t)] = 0 \quad (13)$$

k_e is a radical entry rate coefficient, k_{des} is a desorption rate coefficient and k_{tp} is a radical termination rate constant within the particles, F_i is a number of the particles containing i radical. The complete solution of the equations (12) and (13) can be obtained in the work of Gangwar [5].

III. VALUES OF VARIOUS PARAMETERS USED IN SIMULATION

A. Methyl Methacrylate

$$MW_M = 100.13 \text{ g/mol}$$

$$\rho_m = 0.919 \text{ g/cm}^3$$

$$\rho_p = 1.19 \text{ g/cm}^3$$

$$\phi_{sat} = 0.73$$

$$M_{sat} = 1.56 \times 10^{-4} \text{ mol/cm}^3$$

$$k_p = 2.5119 \times 10^9 \exp(-22200(J)/R_G T(K)) \text{ cm}^3/\text{gmol s}$$

$$k_{tw} = k_{t0} = 9.8 \times 10^{10} \exp(-2934.4(J)/R_G T(K)) \text{ cm}^3/\text{mol s}$$

$$k_t = k_{t0} \exp(-(\beta_1 * w_p + \beta_2 * w_p^2))$$

$$\beta_1 = -41.54 + 0.1082 * T(K)$$

$$\beta_2 = 23.46 - 0.0785 * T(K)$$

$$k_{tr} = 3.41 \times 10^{-5} * k_p$$

$$D_m = 1 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$k_{mp} = 28 \text{ cm/s}$$

$$k_{mm} = \epsilon * k_{mp} \text{ cm/s}$$

$$n = 2$$

B. Sodium Lauryl Sulfate

$$MW_E = 288.33 \text{ g/mol}$$

$$E_{CMC} = 0.0005 \text{ g/cm}^3$$

$$r_m = 2.5 \times 10^{-7} \text{ cm}$$

$$a_{em} = a_{ep} = 50 \times 10^{-16} \text{ cm}^2 \text{ molecule}$$

C. Potassium Persulfate

$$MW_1 = 270.33 \text{ g/mol}$$

$$k_d = 1.5 \times 10^{-6} \text{ s}^{-1} \text{ (at } 50^\circ\text{C)}$$

$$f = 0.5$$

IV. SIMULATION RESULTS AND DISCUSSION

The model simulates an isothermal, well-mixed, semi-batch emulsion polymerization 1-L jacketed glass reactor, equipped with a 4-blade baffle, a flat turbine and an adjustable cooling temperature system. The temperature of the reactor contents was controlled at 50°C with an allowable variation of 0.5°C . At the very beginning of the polymerization, the seeded semi-batch reactor contains some part of monomer (methyl methacrylate = 20% = 30 g) of the total monomer (= 150 g), water (600 g) and emulsifier (sodium dodecyl sulphate) (3.0 g). This reaction mixture is stirred at 350 rpm. After a pre-feed time 10 min, the monomer is fed in the reactor at two different flow rates of 1 g/min and 2 g/min. In figure 1, model predictions for monomer flow rate of 1 g/min and emulsifier amount of 3 g was compared with the experimental data with aqueous phase radical concentration given by RAD1 and RAD2 (these were described earlier). It can be observed that the model predictions for the conversion versus time curve with RAD2 were much closer to experimental data at all times than those with RAD1.

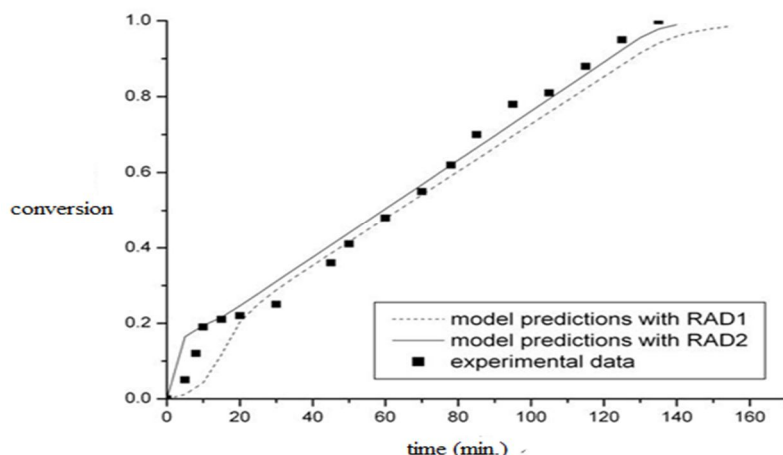


Figure 1: Comparison between the model predictions with experimental data for monomer flow rate of 1 g/min and emulsifier amount of 3 g with RAD1 and RAD2.

In figure 2, the monomer flow rate was 2 g/min and emulsifier amount was 3 g. It can again be observed that the model predictions compared good with the experimental data with RAD2 as compared to RAD1.

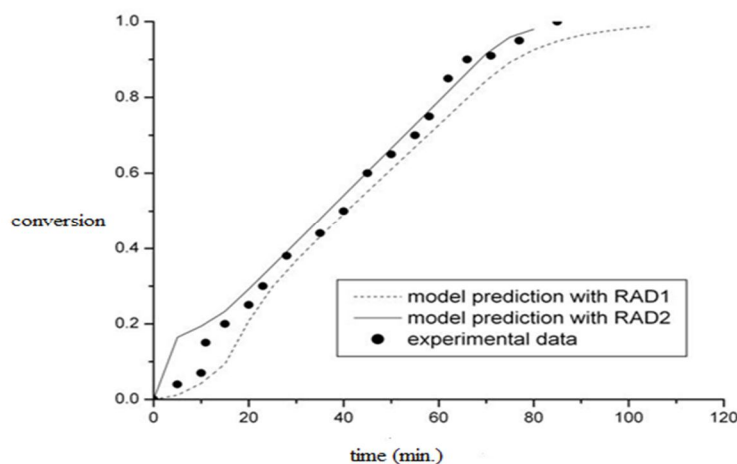


Figure 2: Comparison between the model predictions with experimental data for monomer flow rate of 2 g/min and emulsifier amount of 3 g with RAD1 and RAD2.

V. CONCLUSIONS

In this work, a mathematical model is developed, solved and validated in seeded emulsion polymerization of the methyl methacrylate in the presence of sodium dodecyl sulphate as an emulsifier and potassium persulphate as an initiator. The assumption of the monodisperse distribution of a particle size (sizes of all the particles were same at a given time) is used in developing the model. The model contains mechanistic details such as: (1) The creation of the particle from micellar nucleation mechanisms; (2) Coupling of the radical concentrations in the aqueous phase and the particle phase; (3) Determination of the average number of radicals within the particles by entering into, exiting and termination within the particles with assumption of pseudo bulk kinetics; (4) Gel Effect; (5) Partition of the monomer between the aqueous phase and the particles phase governed by thermodynamic equilibrium, both in presence and absence of monomer droplets. The effect of two different monomer flow rates on the variation of conversion with time was studied by the model. It can be observed that the model predictions compared good with the experimental data with RAD2. The parameters of the model are obtained from the literature and there are no adjustable parameters in the model.



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