SIMULATION OF EMULSION COPOLYMERIZATION REACTIONS IN A CONTINUOUS PULSED SIEVE-PLATE COLUMN REACTOR

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Abstract - This work addressed the viability of using a pulsed sieve-plate column reactor to carry out continuous vinyl acetate/butyl acrylate emulsion copolymerization reactions. A rigorous mathematical model of emulsion copolymerization reactions in a tubular reactor with axial dispersion was used for this purpose. Operational conditions were defined to attain high monomer conversions at the reactor outlet in a relatively short residence time and, at the same time, produce a copolymer with a more homogeneous composition.
Keywords: continuous pulsed sieve-plate column (PSPC), emulsion copolymerization, modeling.

INTRODUCTION

In previous work (Palma et al., 2001a, 2001b; Sayer et al., 2002a, 2002b) a new type of reactor, the pulsed sieve-plate column (PSPC), had been studied for emulsion vinyl acetate homopolymerization reactions. It had been observed that transforming batch emulsion polymerization reactions into continuous reactions in a PSPC may be an attractive way to intensify this process since: 1) high conversions can be achieved in short residence times; 2) the process is safer in the PSPC than in a stirred tank batch or continuous reactor, due to the high heat exchange capacity of the PSPC and 3) due to the continuous operation, variations in product quality, which are commonly found from one batch to the next, are avoided.

In batch copolymerizations carried out with comonomers that have very different reactivity ratios, a copolymer composition drift is observed during the reaction (Araújo, 1997). This same behavior is also observed in continuous reactions in tubular reactors that are not perfectly mixed. Van den Boomen et al. (1999) and Scholtens et al. (2001) conducted experimental studies of styrene/methyl acrylate emulsion copolymerization reactions (reactivity ratios $r_{Sty/MA} = 0.73$ and $r_{MA/Sty} = 0.19$) in a continuous pulsed column reactor and verified that for this system, which does not show differences in order of magnitude between the reactivity ratios, the copolymer composition can be controlled using lateral monomer feed streams.

This work addresses the viability of using the PSPC for vinyl acetate/butyl acrylate emulsion copolymerization reactions. This system was chosen due to its importance in the paint and paper coatings industries and for having very different reactivity ratios ($r_{VA/BA} = 0.037$ and $r_{BA/VA} = 6.35$). A rigorous
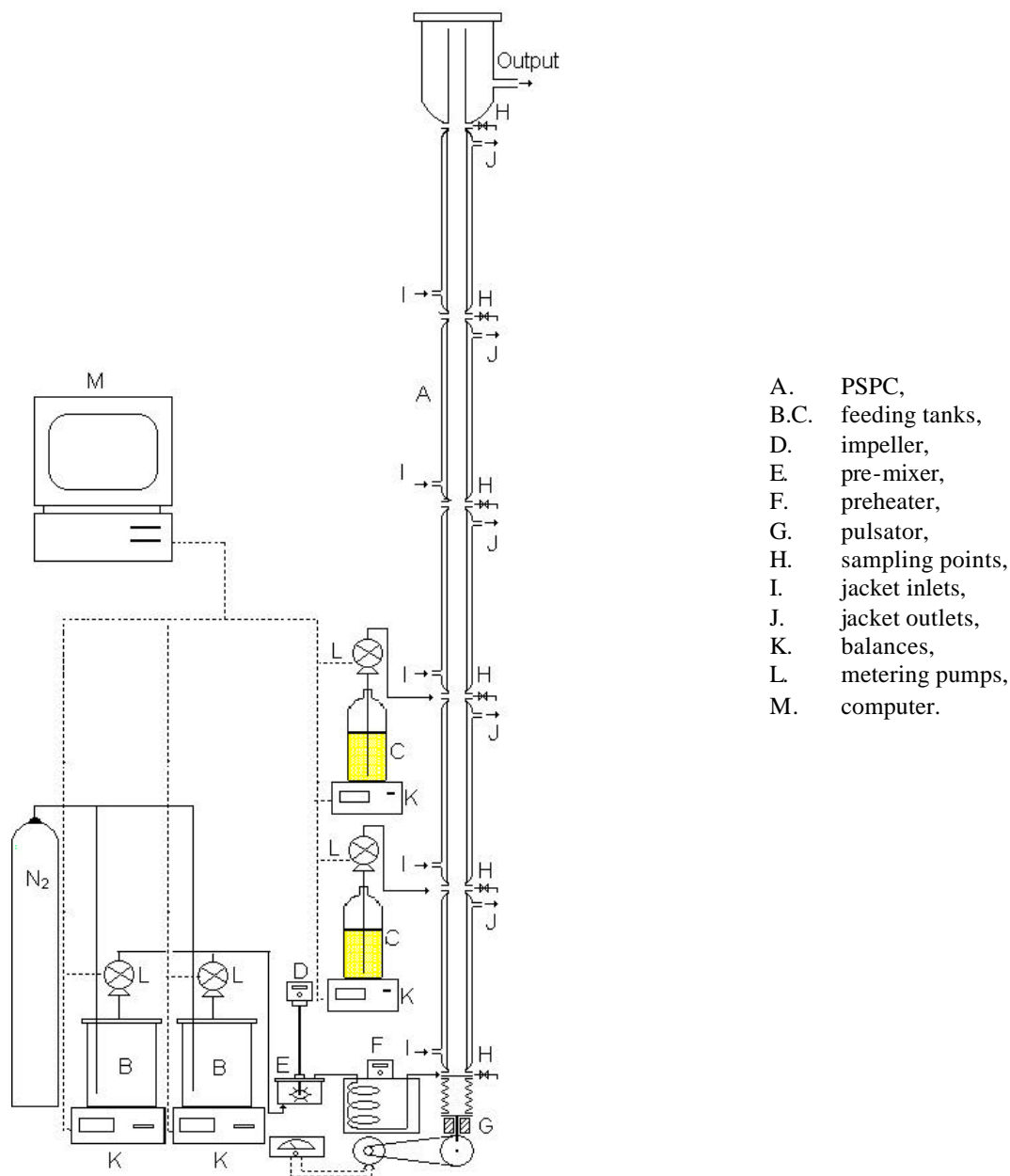
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dynamic mathematical model of emulsion copolymerization reactions was used in this study. The effect of various process variables – axial dispersion, manipulated through the amplitude of the pulses; initiator and emulsifier concentrations; and lateral monomer feed streams – on conversion and copolymer composition was verified.

DESCRIPTION OF THE PSPC REACTOR

The PSPC (Figure 1) is composed of five stainless steel sections, each one with a length of

1000 mm and an internal diameter of 40.0 mm. The plates are stainless steel disks, each with 39 3 mm holes in a triangular arrangement, resulting in a free area of 22.3% on each plate. Plate spacing is 50 mm, resulting in a free volume of 95.7% of the reactor.

In order to prevent demulsification and the consequent plugging of the reactor, a pulsation is superposed on the nominal axial flow. The pulsator is located at the bottom of the column and the stroke length and pulsation frequency may be adjusted within the ranges of 5 to 25 mm and 0.2 and 3.5 Hz, respectively. Reactants are fed in the bottom and at points throughout the PSPC.

A.   PSPC,
B.C. feeding tanks,
D.   impeller,
E.   pre-mixer,
F.   preheater,
G.   pulsator,
H.   sampling points,
I.   jacket inlets,
J.   jacket outlets,
K.   balances,
L.   metering pumps,
M.   computer.

Figure 1: Diagram of the experimental setup:

MATHEMATICAL MODELING

The mathematical model is based on a previous model of Sayer et al. (2002a) of emulsion homopolymerization reactions in the PSPC. In the elaboration/complementation of this model the following assumptions are made:

- Monomer concentrations in polymer particles, monomer droplets and aqueous phase are at thermodynamic equilibrium and are computed using the iterative procedure proposed by Omi et al. (1985).
- Total mass of polymer produced in the aqueous phase is negligible.
- Particle nucleation occurs through micelar and homogeneous mechanisms.
- Particle coagulation depends on initiator concentration.
- The average number of radicals per polymer particle is computed using the method proposed by Ugelstad et al. (1967).
- Polymer particles are spherical and monodisperse.
- The critical micelar concentration and the surface covered by one mol of emulsifier are constant.
- The pseudo-steady-state assumption is valid for polymer radicals.
- Kinetic constants do not depend on chain length.
- Kinetic constants in the aqueous and polymer phases are the same.
- Radicals generated by initiation or chain transfer to monomer and polymer have similar reactivities.
- Reactions are conducted at constant temperature.
- Radial mixing is perfect.
- Average net forward velocity is constant.
- Axial mixing is represented by an effective axial dispersion coefficient.
- The boundary conditions of Danckwerts (1953) were applied to the axial dispersion model.
- The method of lines was used to solve the second-order partial differential equations.

The balance equations of continuous homopolymerization reactions in the PSPC were presented in Sayer et al. (2002a) and are shown in the Appendix. In the present work the following average coefficients were used to describe the copolymerization reactions:

Propagation:

$$k_p \left[M \right]_p = \sum_{i=A,B} \left(k_{pAi} P_{Ap} + k_{pBi} P_{Bp} \right) \left[i \right]_p \qquad (1)$$

Chain transfer to monomer:

$$k_f \left[M \right]_p = \sum_{i=A,B} \left(k_{fAi} P_{Ap} + k_{fBi} P_{Bp} \right) \left[i \right]_p \qquad (2)$$

Termination:

$$k_t = k_{tAA} \, P_{Ap}^{\ 2} + 2k_{tAB} \, P_{Ap} \, P_{Bp} + k_{tBB} \, P_{Bp}^{\ 2} \qquad (3)$$

where P_{Ap} and P_{Bp} are the probabilities that the radicals contain monomeric units of type A or B at the active extremity. All other variables are described in the Appendix.

The model developed was implemented in FORTRAN and differential and algebraic equations were solved by the DASSL solver (Petzold, 1982). The model had been validated previously with experimental data on vinyl acetate emulsion homopolymerization reactions conducted at 55°C in the PSPC (Sayer et al., 2002a). All simulations were carried out using the method of lines with 50 internal points evenly distributed in the axial direction.

RESULTS AND DISCUSSION

In order to evaluate how the butyl acrylate comonomer affects the kinetics of vinyl acetate emulsion polymerization reactions, the results of a vinyl acetate/butyl acrylate copolymerization reaction were compared with those of vinyl acetate (VA) and butyl acrylate (BA) homopolymerization reactions (see formulations in Table 1). In the copolymerization 15 wt.% of monomer is composed of butyl acrylate. Tables 2 and 3 show the operational conditions and the kinetic constants and parameters used in the simulations.

Table 1: Formulation of VA/BA emulsion homo- and copolymerization reactions.

Reactant	VA	BA	VA/BA
	Mass fraction		
VA	0.1878	–	0.1596
BA	–	0.1878	0.0282
Water	0.8069	0.8069	0.8069
SLS	0.0024	0.0024	0.0024
$Na_2S_2O_8$	0.0029	0.0029	0.0029

Table 2: Operational conditions.

Temperature (°C)	55
Residence time (min.)	30
Stroke length (mm)	5
Peclet number	92

## Table 3: Parameters used in the simulations (A - vinyl acetate/B - butyl acrylate).

Parameter	Value	Reference
k_d (1/s)	$1.8.10^{17}\exp[-17155/T]$	Rawlings and Ray, 1988
k_{pAA} (cm^3/mol s)	$1.445.10^{10}\exp[-2490/T]$	Hutchinson et al., 1995
k_{pBB} (cm^3/mol s)	$2.73.10^{9}\exp[-3170/T]$	McKenna et al., 1995
k_{pAB} (cm^3/mol s)	k_{pAA}/r_A	
k_{pBA} (cm^3/mol s)	k_{pBB}/r_B	
k_{fAA} (cm^3/mol s)	$2.43.10^{-4}k_{pAA}$	Chatterjee et al., 1977
k_{fBB} (cm^3/mol s)	$1.9.10^{-4}k_{pBB}$	Brandrup and Immergut, 1989
k_{fAB} (cm^3/mol s)	k_{fAA}/r_A	
k_{fBA} (cm^3/mol s)	k_{fBB}/r_B	
k_{tAA} (cm^3/mol s)	$5.255.10^{9}\exp[-884/T]$	Baad et al., 1982
k_{tBB} (cm^3/mol s)	$1.680.10^{7}\exp[-1409/T]$	McKenna et al., 1995
k_{tAB} (cm^3/mol s)	k_{tAA}	
a_s (cm^2/mol)	$57.10^{-16}N_A$	Min and Ray, 1978
r_m (cm)	$2.5.10^{-7}$	Min and Ray, 1978
$[E]_{CMC}$ (mol/cm^3)	$2.43.10^{-6}$	Unzueta and Forcada, 1997
D_{WA} (cm^2/s)	$1.1.10^{-5}$	Min and Ray, 1978
D_{WB} (cm^2/s)	$1.0.10^{-5}$	Gardon, 1968
D_{pA} (cm^2/s)	$1.1.10^{-6}$	Min and Ray, 1978
D_{pB} (cm^2/s)	$1.0.10^{-7}$	Gardon, 1968
f_{absA}	$3.3.10^{-3}$	-
f_{absB}	$1.0.10^{-5}$	-
f_{absmA}	$1.0.10^{-5}$	-
f_{absmB}	$1.0.10^{-7}$	-
c_{cA}^{0} (1/s)	$4.0.10^{-26}$	-
c_{cB}^{0} (1/s)	0.0	-
c_{homA}^{0} (1/s)	$3.0.10^{-3}$	-
c_{homB}^{0}(1/s)	$1.0.10^{-5}$	-
j_{critA}	16	Gilbert, 1995
j_{critB}	8	Gilbert, 1995
j_{zA}	8	Gilbert, 1995
j_{zB}	1	Gilbert, 1995
PM_A (g/mol)	86.09	Brandrup and Immergut, 1989
PM_B (g/mol)	128.17	Brandrup and Immergut, 1989
PM_E (g/mol)	288.38	Brandrup and Immergut, 1989
PM_w (g/mol)	18.01	Perry and Chilton, 1980
ρ_{mA} (g/cm^3)	0.933	Brandrup and Immergut, 1989
ρ_{mB} (g/cm^3)	0.8	Brandrup and Immergut, 1989
ρ_{pA} (g/cm^3)	1.13	Araújo et al., 2000
ρ_{pB} (g/cm^3)	0.933	Brandrup and Immergut, 1989
ρ_w (g/cm^3)	1.028	Perry and Chilton, 1980
k_A^{d}	34.7	Gardon, 1968
k_B^{d}	705.0	Unzueta and Forcada, 1997
k_A^{p}	29.5	Gardon, 1968
k_B^{p}	460.0	Unzueta and Forcada, 1997
r_A	0.037	Gugliotta et al., 1995
r_B	6.35	Gugliotta et al., 1995

A Comparison of VA/BA Homo- and Co-Polymerization Reactions

Figure 2a compares the evolution of the overall conversions in the PSPC during emulsion VA/BA (85/15) copolymerization and VA and BA homopolymerization reactions. It can be observed that while in the VA and BA homopolymerizations conversions above 95% are reached at the reactor outlet, in the VA/BA (85/15) copolymerization the conversion at the reactor outlet is below 20%. This occurs because the more reactive monomer in this copolymerization (BA) acts as a retardant of the propagation of the other monomer (VA). This can be

verified in Figure 2b, which shows the evolution of the VA and BA fractional conversions in the PSPC during VA/BA (85/15) emulsion copolymerization reactions.

The significant reduction in the reaction rate of the copolymerization reaction compared to those of the copolymerizations may jeopardize this type of reactions in the PSPC, since very long residence times would be required in order to achieve complete monomer conversion. Therefore, in order to enhance the reaction rate, simulations presented below were carried out using a new reaction formulation with higher emulsifier and initiator concentrations, as shown in Table 4.
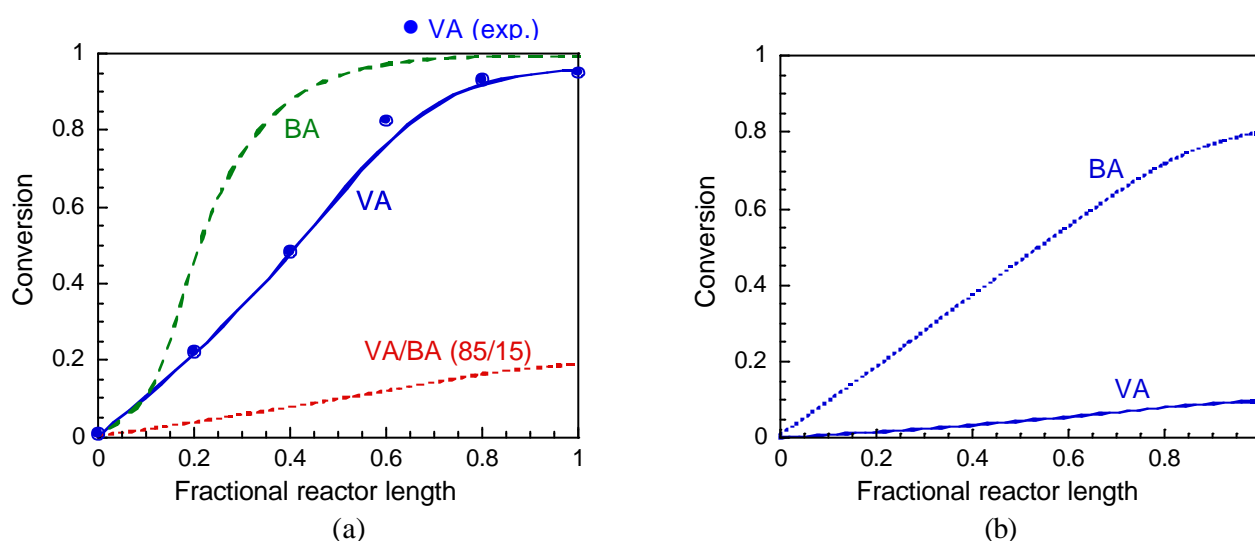
Figure 2: Conversions in the PSPC during VA and BA emulsion homo- and copolymerization reactions. (a) Overall conversions; (b) Fractional conversions.

Table 4: New formulation of VA/BA emulsion copolymerization reactions.

Reactant	Mass fraction
VA	0.1576
BA	0.0279
Water	0.7969
SLS	0.0119
$Na_2S_2O_8$	0.0057

Figure 3a shows the evolution of overall and fractional conversions in the reactor of a reaction carried out in the PSPC using the new formulation. It might be observed that by increasing emulsifier and initiator concentrations, it is possible to reach high conversions in a relatively low residence time. On the other hand, copolymer composition (Figure 3b) shows a significant drift along the reactor length,

resulting in the production of a quite heterogeneous copolymer.

The effect of Axial Dispersion

Figure 4a shows the effect of axial dispersion, which is varied through the Peclet number (Pe), on the composition of the copolymer formed in the

PSPC. It might be observed that a copolymer with a constant composition is only formed when the reactor is operated under conditions that are close to those of perfect mixing (Pe = 0.14). Nevertheless, those conditions result in very low conversions, as shown in Figure 4b, which shows the effect of Pe on conversion in the PSPC.

The effect of Lateral Feed Streams

A way of minimizing the copolymer composition drift along the reactor length without significantly affecting the conversion is to use lateral feed streams of the more reactive monomer.
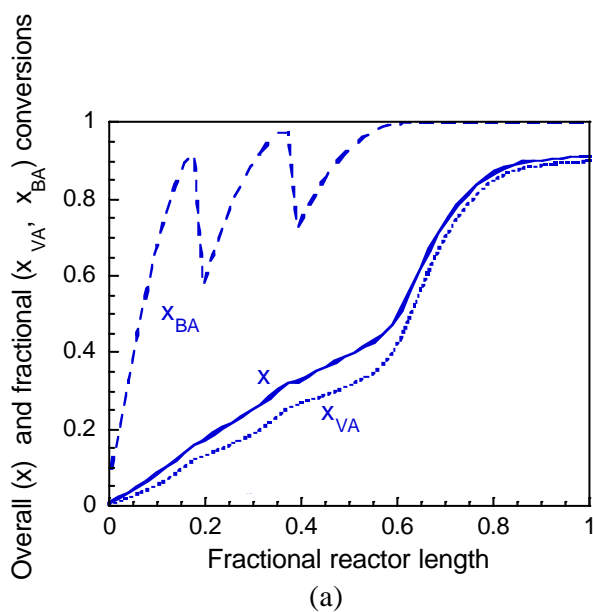
Figures 5a and b show the evolution of overall and fractional conversions and copolymer composition in the PSPC of a reaction performed with two lateral BA feed streams. It might be observed that with this procedure the copolymer composition shows a much less accentuated drift in the reactor, resulting in the production of a more homogeneous copolymer.
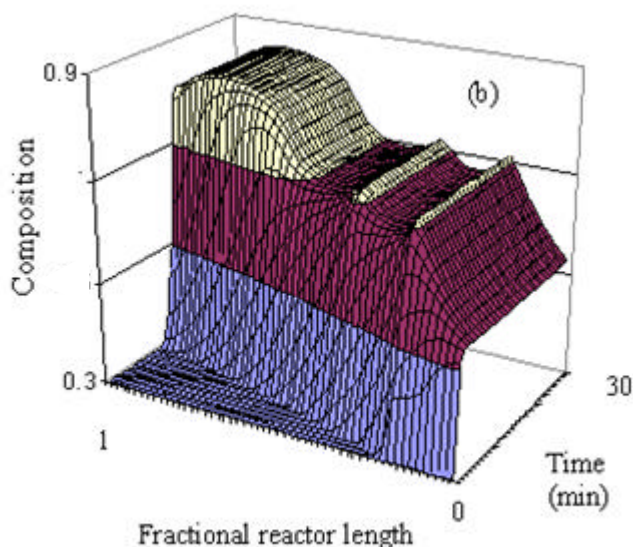

(a)

(b)
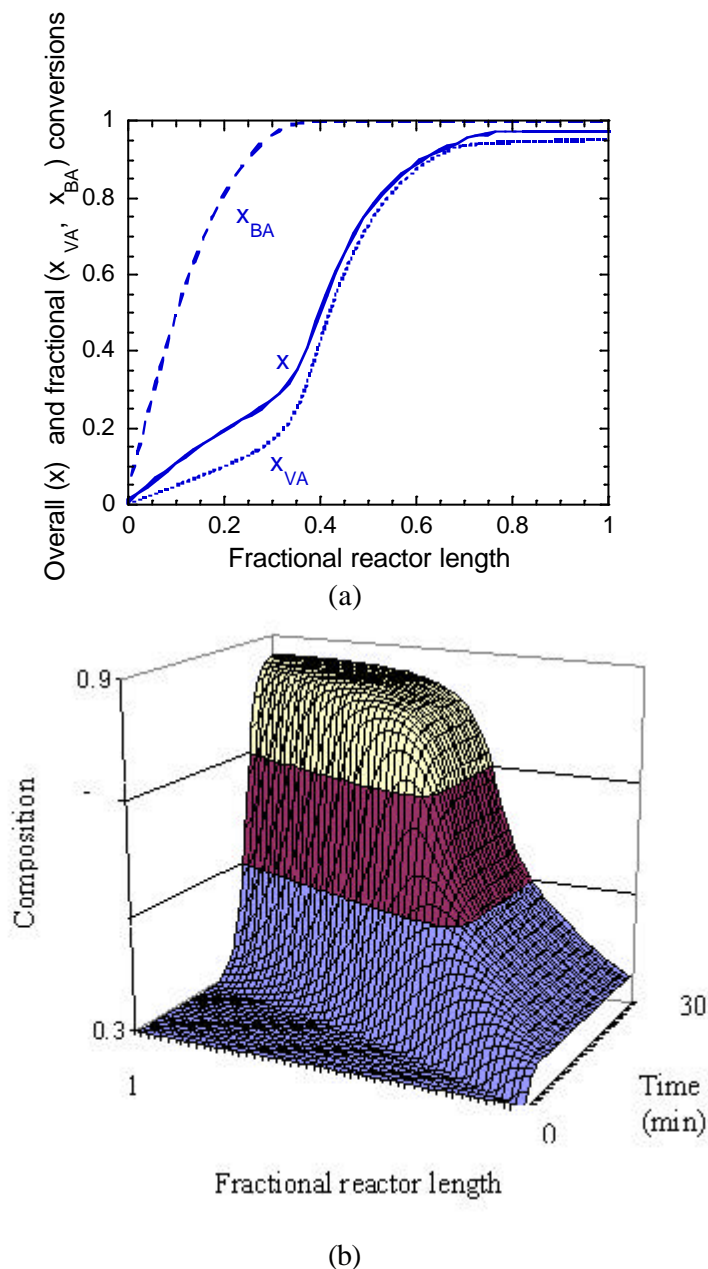
Figure 3: Conversions and copolymer composition in the PSPC during VA and BA emulsion copolymerization reactions − new formulation (Table 4). (a) Overall and fractional conversions; (b) Copolymer composition (mass fraction of VA).

(a)

(b)
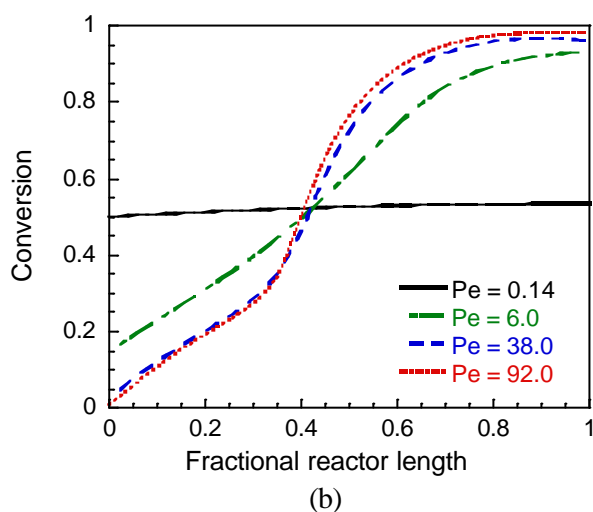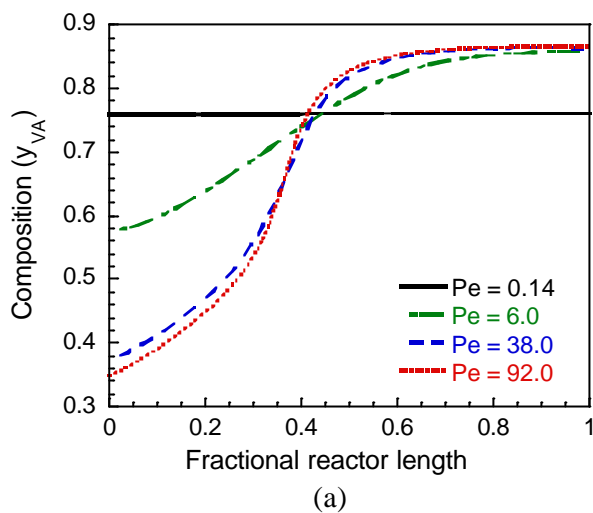
Figure 4: Effect of Peclet number on copolymer composition and overall conversion in the PSPC during VA and BA emulsion copolymerization reactions. (a) Copolymer composition (mass fraction of VA); (b) Overall and fractional conversions.

(a)

(b)

Figure 5: Conversions and copolymer composition in the PSPC during VA and BA emulsion copolymerization reactions with two lateral BA feed streams. (a) Overall and fractional conversions; (b) Copolymer composition (mass fraction of VA).

CONCLUSIONS

This work involved a computational study of vinyl acetate/butyl acrylate emulsion copolymerization reactions in the pulsed sieve-plate column reactor (PSPC). It was observed that due to the significant difference between the reactivity ratios of these two monomers, vinyl acetate/butyl acrylate emulsion copolymerization reactions are significantly slower than the vinyl acetate or butyl acrylate copolymerization reactions carried out under the same operational conditions. Therefore, a new formulation with higher initiator and emulsifier concentrations was tested. With this new formulation it was possible to achieve high conversions (~100%) in a relatively low residence time (30 minutes). Nevertheless, also due to the significant difference between the reactivity ratios of these two monomers, the copolymer composition showed a considerable drift along the reactor length, thereby resulting in a quite heterogeneous copolymer. It was verified that this composition drift can be minimized using lateral feed streams of the more reactive monomer in the copolymerization, in this case the butyl acrylate.

ACKNOWLEDGEMENTS

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APPENDIX

EQUATIONS OF THE EMULSION POLYMERIZATION MODEL

In order to model continuous reactions carried out in the PSPC, a dynamic axially dispersed plug-flow model was implemented. Given the assumptions shown in Section 3, the population and mass balance equations for a continuous emulsion polymerization system are presented below:

a) Polymer Particle Concentration - N_p

$$\frac{\partial N_p}{\partial t} + v_z \frac{\partial N_p}{\partial z} - De \frac{\partial^2 N_p}{\partial z^2} = \\ = R_{mic} + R_{hom} - c_c (N_p)^2 \tag{A1}$$

where v_z is the axial velocity and De is the effective dispersion coefficient in cm^2/s and

$$v_z = \frac{q_e}{\left(\pi r_{col}^2 f_{void}\right)} \tag{A2}$$

$$De = v_z \frac{a_{col}}{Pe} \tag{A3}$$

where q_e is the inlet flow rate of the reactor in cm^3/s; r_{col} and a_{col} are, respectively, the radius and the length of the PSPC in cm and f_{void} is the void fraction of the PSPC. Pe is the Peclet number, R_{mic} and R_{hom} represent the micelar and homogeneous nucleation rates and $c_c (N_p)^2$ represents the rate of particle coalescence.

Micelar nucleation:

$$R_{mic} = k^m_{abs} R_{ent} N_{mic} \tag{A4}$$

where R_{ent} is the concentration of radicals in the aqueous phase that may enter polymer particles and k^m_{abs} is the absorption rate coefficient of radicals from the aqueous phase by the micelles given by the Smoluchowski equation:

$$k^m_{abs} = 4\pi D_w r_m Na f^m_{abs} \tag{A5}$$

where D_w, r_m and f^m_{abs} represent, respectively, the diffusion coefficient in the aqueous phase, the radius of one micelle and the absorption efficiency of radicals from the aqueous phase by the micelles.

Variable N_{mic} is the concentration of micelles formed when the emulsifier concentration in the aqueous phase $[E]^{aq}$ is above the critical micelar concentration (CMC):

$$N_{mic} = M_{mic} v_{aq} \tag{A6}$$

where M_{mic} is the number of micelles per volume of the aqueous phase and v_R, v_p and v_{aq} are, respectively, the volumes of the reactor and of the polymer and aqueous phases.

Homogeneous nucleation:

$$R_{hom} = c_{hom}{}^0 k_p [M]_{aq} R_{jcrit} Na v_{aq} \tag{A7}$$

where $c_{hom}{}^0$ is the coefficient of homogeneous nucleation and $k_p[M]_{aq}$ is the propagation rate in the aqueous phase.

Variable R_{jcrit} is the concentration of radicals with the critical length j_{crit} in the aqueous phase.

Particle coalescence:

In order to avoid using rather complex mathematical expressions like the extensions of the DLVO model (Derjaguin-Landau-Verwey-Overbeek) that involve a significant number of often unknown parameters (Gilbert, 1995; Araújo et al., 2000), a simple equation for the rate constant of particle coalescence was used. This equation is an extremely simplified version of the DLVO model and the only effect that is accounted for in this equation is the initiator concentration in the aqueous phase, since increasing electrolyte concentrations enhances the particle coagulation rate (Melis et al., 2000):

$$c_c = c_c^0 \sqrt{[I] v_R Na} \tag{A8}$$

where c_c^0 is the only unknown parameter that must be adjusted in order to represent experimental data.

b) Initiator Concentration in the Reactor - [I]

$$\frac{\partial [I]}{\partial t} + v_z \frac{\partial [I]}{\partial z} - De \frac{\partial^2 [I]}{\partial z^2} = -[I] k_d \tag{A9}$$

c) Emulsifier Concentration in the Reactor - [E]

$$\frac{\partial [E]}{\partial t} + v_z \frac{\partial [E]}{\partial z} - De \frac{\partial^2 [E]}{\partial z^2} = 0 \qquad (A10)$$

In emulsion polymerization systems the emulsifier might be in three different forms: a) free in the aqueous phase ($[E]^{aq}$); b) in the form of micelles in the aqueous phase (M_{mic}); and c) adsorbed on polymer particles ($[E]_{ads}$) and monomer droplets. As monomer droplets are significantly larger than polymer particles, they have a much smaller total surface area and, therefore, the amount of emulsifier adsorbed on monomer droplets might be neglected and

$$[E] = \frac{[E]^{aq} v_{aq} + \gamma M_{mic} v_{aq} + a_p N_p [E]_{ads}}{v_R} \qquad (A11)$$

where $[E]^{aq}$ is the concentration of emulsifier in the aqueous phase, γ is the number of moles of emulsifier per micelle and $[E]_{ads}$ is the emulsifier adsorbed on polymer particles per unit surface. Variable γ is computed by

$$\gamma = \frac{4\pi r_m^2}{a_s} \qquad (A12)$$

where a_s is the area covered by one mol of emulsifier and a_p is the surface area of one polymer particle swollen with monomer:

$$a_p = 4\pi r_p^2 \qquad (A13)$$

r_p is the radius of one polymer particle swollen with monomer, computed by

$$r_p = \sqrt[3]{\frac{3 v_p / (N_p v_R)}{4\pi}} \qquad (A14)$$

Variables $[E]^{aq}$, $[E]_{ads}$ and M_{mic} must be computed for three different situations: a) the emulsifier concentration is above the critical micelar concentration ($[E]_{CMC}$), so the emulsifier concentration in the aqueous phase ($[E]^{aq}$) equals $[E]_{CMC}$, the emulsifier concentration adsorbed on polymer particles ($[E]_{ad}$) equals the saturation concentration ($[E]^{sat}_{ads}=1/a_s$) and M_{mic} is computed with Eq. (A11); b) the emulsifier concentration is

below $[E]_{CMC}$ and the emulsifier concentration is large enough to saturate polymer particles, so M_{mic} equals zero, $[E]_{ad}$ equals $[E]^{sat}_{ads}$ (assuming that the emulsifier is absorbed on polymer particles than in the aqueous phase) and $[E]^{aq}$ is computed with Eq. (A11); or c) the emulsifier concentration is below $[E]_{CMC}$ and the emulsifier concentration is not high enough to saturate polymer particles, so M_{mic} and $[E]^{aq}$ equal zero and $[E]_{ad}$ is computed with Eq. (A11).

d) Monomer Concentration in the Reactor - [M]

$$\frac{\partial [M]}{\partial t} + v_z \frac{\partial [M]}{\partial z} - De \frac{\partial^2 [M]}{\partial z^2} = \qquad (A15)$$
$$-\frac{\bar{n} N_p}{Na}\left(k_p [M]_p + k_f [M]_p\right)$$

$[M]_p$ is the monomer concentration in polymer particles. The monomer concentrations in the different phases in emulsion polymerization reactions were computed by the iterative procedure proposed by Omi et al. (1985).

e) Polymer mass in the reactor - P:

$$\frac{\partial P}{\partial t} + v_z \frac{\partial P}{\partial z} - De \frac{\partial^2 P}{\partial z^2} = \frac{\bar{n} N_p}{Na} k_p [M]_p P M_m \qquad (A16)$$

f) Water Fraction in the Reactor - $\boldsymbol{f}_w$:

$$\frac{\partial \boldsymbol{f}_w}{\partial t} + v_z \frac{\partial \boldsymbol{f}_w}{\partial z} - De \frac{\partial^2 \boldsymbol{f}_w}{\partial z^2} = 0 \qquad (A17)$$

g) Computation of the Average Number of Radicals Per Polymer Particle

The method proposed by Ugelstad et al. (1967) was used for the iterative computation of the average number of radicals per polymer particle $\bar{n}$:

$$\bar{n} = \frac{1}{2}\cfrac{h^2/4}{m + 0 + \cfrac{h^2/4}{m + 1 + \cfrac{h^2/4}{m + 2 + \ldots}}} \qquad (A18)$$

where h and m are the relative absorption/termination and desorption/termination coefficients, defined as

$$h = \left(\frac{8k_{abs}R_{ent}Nav_p}{k_t \, xgelN_p v_R} \right)^{\frac{1}{2}} \qquad (A19)$$

$$m = \frac{kNav_p}{k_t \, xgelN_p v_R} \qquad (A20)$$

k_{abs} is the coefficient of the rate of absorption of radicals from the aqueous phase by the polymer particles, given by the Smoluchowski equation:

$$k_{abs} = 4\pi D_w r_p Naf_{abs} \qquad (A21)$$

where R_{ent} is the concentration of radicals in the aqueous phase that may enter polymer particles. R_{ent} is computed by the iterative procedure developed by Araújo et al. (2000) based on two different critical radical lengths proposed by Gilbert (1995):

$$\Psi = k_p[M]_{aq} + k_{abs}\frac{N_p v_R}{v_{aq}Na} +$$

$$+k^m{}_{abs}\frac{N_{mic}v_R}{v_{aq}Na} + k_t R_{aq} \qquad (A22)$$

$$R_1 = \left(\frac{\dfrac{2Iv_R fk_d}{v_{aq}} + \dfrac{k \, \overline{n} N_p v_R}{v_{aq}Na}}{k_p[M]_{aq} + k_t R_{aq}} \right) \qquad (A23)$$

$$R_{jcrit} = R_1 \left(\frac{k_p[M]_{aq}}{k_p[M]_{aq} + k_t R_{aq}} \right)^{(j_z-2)}$$

$$\left(\frac{k_p[M]_{aq}}{\Psi} \right)^{(j_{crit}-j_z)} \qquad (A24)$$

$$R_{ent} = R_1 \left(\frac{k_p[M]_{aq}}{k_p[M]_{aq} + k_t R_{aq}} \right)^{(j_z-2)} \qquad (A25)$$

$$\sum_{j=j_z}^{jcrit-1} \left(\frac{k_p[M]_{aq}}{\Psi} \right)^{(j-j_z+1)}$$

$$R_{aq} = R_1 \left[1 + \sum_{j=2}^{j_z-1} \left(\frac{k_p[M]_{aq}}{k_p[M]_{aq} + k_t R_{aq}} \right)^{(j-1)} \right] + R_{ent} \qquad (A26)$$

where R_{aq} is the concentration of radicals in the aqueous phase; j_z and j_{crit} are the critical lengths for radical entry into micelles and polymer particles and for homogeneous nucleation (Gilbert, 1995), which depend on the solubility of the monomer in the aqueous phase; $k_t R_{aq}$ and $k_p[M]_{aq}$ are termination and propagation rates in the aqueous phase per unit radical; f is the efficiency in forming radicals by decomposition of the initiator and k is the coefficient of the rate of desorption of radicals from polymer particles:

$$k = k_f[M]_p \frac{k_{0m}}{\left(k_{0m}\beta_m + k_p[M]_p \right)} \qquad (A27)$$

where k_{0m} and β_m are the exit rate of a monomeric radical from a polymer particle and the probability that a radical in the aqueous phase will react by propagation or by termination:

$$k_{0m} = \frac{3\dfrac{D_w}{r_p{}^2 k_m^p}}{2\dfrac{D_w}{D_p k_m{}^p}+1} \qquad (A28)$$

$$\beta_m = \frac{\left(k_p[M]_w + k_t R_{aq} \right)}{(\psi)} \qquad (A29)$$

where D_p is the diffusion coefficient of a radical in polymer particles in cm^2/s.