Effects of Mixing on the Formation of Polymer Particles in Suspension Polymerization

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A population balance model is presented for suspension polymerization of vinyl chloride in an isothermal batch reactor mixed perfectly on macrolevel. Coalescence and breakage of monomer droplets, as well as micromixing of species between the droplets induced by coalescence are also included into the model, forming a complex three-scale system. The resulted population balance equation is solved by coupling solution of the deterministic polymerization reactions with Monte Carlo simulation of coalescence-breakage discrete events. The results obtained by simulation show that micromixing of species induced by droplets coalescence affects the process significantly.

1. Introduction

Suspension polymerization is an often used method for producing such important polymers as polystyrene and polyvinyl chloride on industrial scale. In this method, the monomer is initially dispersed in the aqueous phase by intensive stirring and adding suspension stabilizers, and polymerization occurs in the monomer droplets as the initiator is dissolved in the monomer phase.

Polyvinyl chloride is produced by powder polymerization since the polyvinyl chloride is insoluble in the vinyl chloride monomer hence it almost immediately precipitates out formatting a separate phase and irregular grains. However, in suspension polymerization the monomer droplets break-up and coalesce continuously in the turbulent flow field generated by intensive stirring. As this breakage-coalescence process of drops proceeds parallel with polymerization inside the droplets their interactions may have significant effects on the final particle size distribution what is one of the most important issues in suspension polymerization (Hashim and Brooks, 2004; Kotoulas and Kiparissides, 2006).

The population balance approach can be applied describing the temporal evolution of drop size distribution adequately (Kotoulas and Kiparissides, 2006). In modeling suspension polymerization, however, applying this approach requires solving the population balance equation, describing the drop size distribution, simultaneously with computing the polymerization reactions occurring inside the droplets. In addition, during the course of coalescence of drops some equalization of species, i.e. micromixing takes place what complicates the problem even more. Taking into consideration the random nature of breakage-coalescence and micromixing processes Monte Carlo simulation seems to be a suitable method for solving this crucial numerical problem.

The aim of the paper is to present and analyze the suspension polymerization process of

vinyl chloride with taking into account breakage and coalescence of droplets as well as micromixing induced by coalescence applying the Monte Carlo method. In the model, binary breakage-coalescence events are assumed, while the kinetic data of vinyl chloride polymerization are taken from the literature (De Roo et al., 2005). The process, assumed to be isothermal, is discussed and analyzed by simulation.

2. Suspension polymerization of vinyl chloride

In suspension polymerization of vinyl chloride the monomer is insoluble in water so that suspending it in the aqueous phase forms small droplets by vigorous mixing. The initiators are soluble in the monomer therefore adding some initiator into the suspension it becomes mixed randomly with the monomer.

The suspension polymerization process of vinyl chloride exhibits three stages (Xie et al., 1991; De Roo et al., 2005). Each stage is characterized by a number of phases present in the polymerization reactor. During the first stage polymerization occurs in the monomer phase, called monomer-rich phase. Because the polymer is almost insoluble in its monomer, it almost immediately forms a separate phase called polymer-rich phase. This second stage starts at a monomer conversion of about 0.1 %. During the second stage, polymerization proceeds in both the monomer-rich and poly-mer-rich phases. The polymer molecules that are formed in the monomer-rich phase are transferred to the polymer-rich phase, leading to constant composition of this phase up to approximately 30 wt% of monomer. This composition is determined by the solubility of monomer in the polymer-rich phase. Due to the constant composition of polymer-rich phase and increasing conversion of vinyl chloride, the monomer-rich phase decreases in volume while the polymer-rich phase volume increases. At a conversion of about 65 %, named critical conversion, the monomer-rich phase disappears and the third stage starts. Then, polymerization takes place in the polymer-rich phase only, the composition of which now changes due to the further conversion of monomer. As a result the viscosity of this phase increases notably.

The model regarding the process time is divided into two sub-processes. In the first part, when conversion is less than the critical one, the monomer concentration in the drops proves to be constant. When the conversion is higher than the critical one polymer crusts evolve in the drops which practically prevent material transport between the drops. So the monomer concentration will start to decrease in the drops and, in addition, the volume of drops remains constant.

The reactions accounting for the vinyl chloride suspension polymerization are summarized in Table 1.

The reaction scheme presented in Table 1 was used in both parts of polymerization process. The corresponding mass balance equations were solved by using the rate coefficients published by De Roo et al. (2005), applying appropriate modifications accounting for the viscous differences of phases.

3. Model developments

Let us assume that a batch, agitated suspension polymerization reactor of vinyl chloride

Table 1: Vinyl chloride polymerization reactions used in simulation

Decomposition of the initiator:	$I \xrightarrow{k_d} 2I^*$		
Chain initiation:	$I^* + M \xrightarrow{k_d} R_1$		
Propagation:	$R_1 + M \xrightarrow{k_p} R_2$	$R_2 + M \xrightarrow{k_p} R_3$	
Chain transfer:	$R_1 + M \xrightarrow{k_{tM}} R_1 + P_1$		
Termination:	$R_i \xrightarrow{k_t} P_i$	$R_i + R_j \xrightarrow{k_{tc}} P_{i+j}$	$R_i + R_j \xrightarrow{k_{td}} P_i + P_j$

is perfectly mixed on macrolevel, i.e. the monomer drops, stabilized with some surface-active agent are distributed evenly in the continuous aqueous phase of the reactor. The initiator, soluble in the monomer is distributed in the droplets by intensive turbulent stirring, inducing simultaneously an initial breakage and coalescence process of drops. As the reactor is heated to the polymerization temperature the polymerization process is started under isothermal conditions and subsequently two processes occur parallel in the reactor. Polymerization reactions, having rates depending on the actual states of phases and concentrations inside the droplets form a continuous in time deterministic process, as well as coalescence and breakage of drops with micromixing in the coalescence state that form a stochastic discrete event process.

Combination of these processes provides a complex three-scale system in which polymerization reactions occur on micro-scale while the discrete event interactions between drops, being meso-scale objects in this system occur on meso-scale. The macro-scale of the system, because the reactor is assumed to be perfectly mixed on macro-level becomes merged into the meso-scale. Then the population balance equation, extended with the mass transfer interaction terms induced by collisions of drops, can be written for this system as (Lakatos, 2010):

$$
\frac{\partial n(v,\boldsymbol{c},t)}{\partial t} + \nabla_{\boldsymbol{c}} \cdot \left[\frac{d\boldsymbol{c}}{dt} n(v,\boldsymbol{c},t) \right] = -n(v,\boldsymbol{c},t)\alpha_b(v) + \int\limits_{v}^{v_m} \beta_b(v,\upsilon)\alpha_b(\upsilon)n(\upsilon,\boldsymbol{c},t)\,d\upsilon
$$

$$
- S_{eff} \int\limits_{0}^{c_m}\int\limits_{0}^{c_m}\int\limits_{0}^{v_m} \beta_a(v,\upsilon)\delta\!\left(\boldsymbol{c}'' - \frac{\boldsymbol{c}+\boldsymbol{c}'}{2} \right) n(v,\boldsymbol{c},t)n(\upsilon,\boldsymbol{c}',t)\,d\upsilon d\boldsymbol{c}' \tag{1}
$$

$$
+ S_{eff} \int\limits_{0}^{c_m}\int\limits_{0}^{c_m}\int\limits_{0}^{v} \beta_a(v-\upsilon,\upsilon)\delta\!\left(\boldsymbol{c} - \frac{\boldsymbol{c}'+\boldsymbol{c}''}{2} \right) n(v-\upsilon,\boldsymbol{c}',t)n(\upsilon,\boldsymbol{c}'',t)\,d\upsilon + \boldsymbol{M_i^K}[n(v,\boldsymbol{c},t)]
$$

where

$$
\boldsymbol{M_i^K}[n(v,\boldsymbol{c},t)] = -\frac{(1-S_{eff})}{\mu_0(t)} \int\limits_{0}^{c_m}\int\limits_{0}^{c_m}\int\limits_{0}^{v_m}\int\limits_{0}^{1} \beta_a(v,\upsilon) \prod_{k=1}^{k=K} \frac{2^K}{\omega_k} \delta_{c_{k'}} \left[\left(\frac{2(c_{k}{}'-c_k)}{\omega_k} + c_k \right) - c_k{}'' \right] \times
$$

$$
\times F_{\omega}(d\boldsymbol{\omega})n(v,\boldsymbol{c}',t)n(\upsilon,\boldsymbol{c}'',t)\,d\upsilon d\boldsymbol{c}'d\boldsymbol{c}'' + \frac{(1-S_{eff})}{\mu_0(t)} \int\limits_{0}^{c_m}\int\limits_{0}^{c_m}\int\limits_{0}^{v_m}\int\limits_{0}^{1} \beta_a(v,\upsilon) \times \tag{2}
$$

$$\times \prod_{k=1}^{k=K} \frac{2^K}{\omega_k} \delta_{c_k} \left[\left(\frac{2(c_k - c_k')}{\omega_k} + c_k' \right) - c_k'' \right] F_\omega(d\omega) n(v, \mathbf{c}', t) n(v, \mathbf{c}'', t) dv dc' dc'' .$$

On the left hand side of Eq.(1), the second term describes the rate of change of the population density function due to polymerization reactions inside the drops, the first two terms on the right hand side represent the rate of change due to breakage, while the third and fourth terms describe that caused by coalescence. The final terms on the right hand side provide the rate of change of the population density function due to mass exchange between the drops during their impacts by collisions without coalescence.

Since interactions of drops with the aqueous phase are negligible the population balance equation (1) provides a model sufficient for describing the suspension polymerization process. Numerical solution of this multi-dimensional equation seems to a crucial problem but application of the Monte Carlo method for simulation of the coalescence-breakage-micromixing process, exhibiting discrete events nature, has proved to be a suitable method for solution.
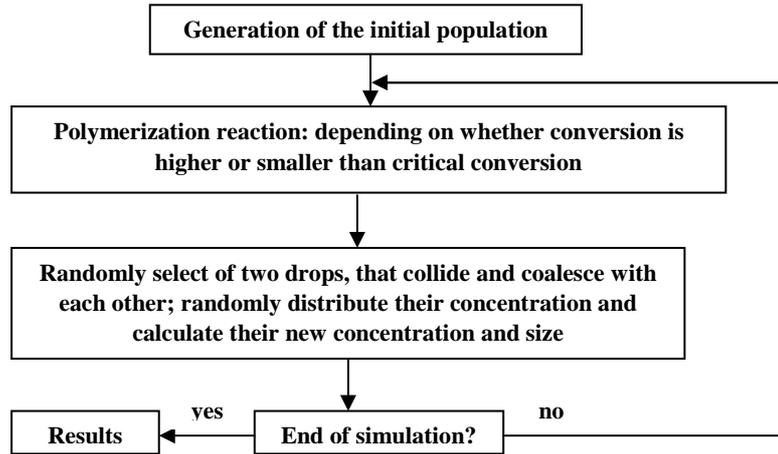

Fig. 1: Algorithm of simulation of suspension polymerization process

4. Simulation results and discussion

A simplified scheme of the algorithm developed for solving Eq.(1) is shown in Fig.1. The corresponding computer program and all simulation runs were written and carried out in MatLab environment.

In simulation runs, a thousand-element drop population was used examining the effects of coalescence-breakage process on the initial size distribution of drops, the influence of the initial distribution of the initiator in the drops, the effects of coalescence-breakage-micromixing process on the history and efficiency of polymerization reactions both inside some marked drops and also the mean values of concentrations and conversions summarized over all drops participating in the suspension polymerization process of vinyl chloride.

At start of simulation runs, the diameter of all drops was assumed 100 μm while the distribution of the same amount of initiator was changed as follows. Namely, the same amount of initiator was evenly distributed in all drops, then only in 100, 250 and 500 drops, as well as randomly in 100 marked drops.

Fig.2 presents the temporal evolution of the mean value of initiator concentration as a function of the initial distribution of initiator. Assuming perfect mixing state on both the micro- and macrolevel the initiator concentration starts to grow at the beginning of the process. This occurs because the rate of decrease of the volume of monomer is larger than that of the number of moles of initiator whilst the polymer is insoluble in monomer. Fig.3 shows evolution of the mean conversion expressed as percentage of the amount of monomer transformed into polymer. The results demonstrate that the mean conversion achieves maximum value when the system is perfectly mixed on both levels and there no any interactions between those. This is not surprising since in this case all drops behave in the system as perfectly mixed micro-reactors.
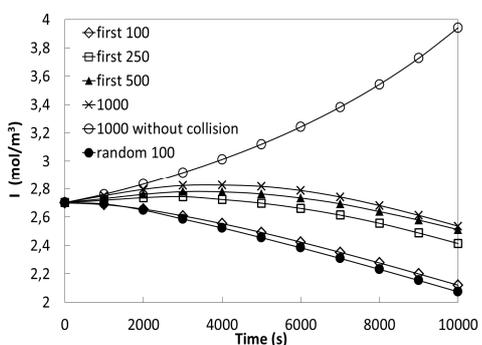

Fig. 2: Evolution in time of the average value of initiator concentration
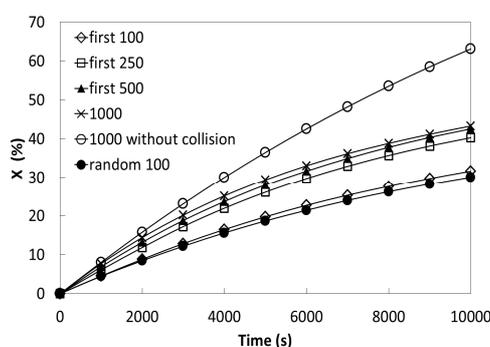
Fig.3: Evolution in time of the mean value of monomer conversion expressed as percentage of amount of monomer transformed into polymer

5. Conclusions

A population balance model was presented for suspension polymerization of vinyl chloride in an isothermal batch reactor mixed perfectly on macrolevel. Coalescence and breakage of monomer droplets, as well as micromixing of species between the droplets induced by coalescence were also included into the model, forming a complex three-scale system. The resulted population balance equation was solved by coupling solution of the deterministic polymerization reactions with Monte Carlo simulation of coalesceence-breakage-micromixing discrete events. The results obtained by simulation show that micromixing of species induced by droplets coalescence affects the process significantly.

Notation

c	vector of concentration variables in a drop	$n(v,c,t)$	population density function of the drop population
$F_{\omega k}$	distribution function	μ_0	total number of drops in a unit volume of suspension
I	initiator	P_i	the closed polymer chain with chain length i
I^*	active initiator radical	R_i	the growing polymer chain with chain length i
k_d	initiator decomposition rate coefficient [1/s]	S_{eff}	effectivity coefficient of coalescence of drops
k_p	propagation rate coefficient [m^3/(mol·s)]	t	time [s]
k_t	rate coefficient of termination [m^3/(mol· s)]	v	drop volume
k_{tM}	chain transfer rate coefficient [m^3/(mol·s)]	α_b	selection function for breakage
k^{th}	species	β_b	breakage function
M	monomer	β_a	frequency of collisions of drops

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