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Modelling and Simulation of a Batch Poly(Vinyl Chloride) Reactor

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A population balance model for batch suspension polymerization of vinyl chloride is presented. Break up into two equal volumes of droplets, binary aggregation and random mass exchanges between the colliding droplets are assumed, while the kinetic data of vinyl chloride polymerization are taken from the literature. The model and the process are analyzed by simulation applying a novel Monte Carlo method taking into account breakage and aggregation of droplets as well as micromixing induced by droplet binary collisions as stochastic discrete event processes. The results revealed that this method of modelling describes phenomena in suspension polymerization of vinyl chloride properly.

1. Introduction

Many chemical processes are based on chemical reactions taking place in stirred tank reactors. These often are two-phase processes, for example, crystallization and suspension or emulsion polymerization. In these processes the particle or drop size distribution beside the heat and mass transfer often affect the product quality significantly.

The droplet size distribution in liquid-liquid processes is generated by different phenomena, which can be divided into diverse categories: feed or discharge of droplets in a particular region of the vessel under consideration, nucleation and growth of droplets as well as breakage and coalescence of droplets.

The size distribution of droplets can be described adequately by means of the population balance approach (Kotoulas and Kiparissides, 2006). In this method, the population balance equation (PBE) is an integral-differential equation governing the temporal evolution of a population density function as a result of different mechanisms forming the particles like nucleation, growth, aggregation and breakage.

The PBE has found a lot of different applications like crystallization, precipitation, aerosol dynamics, microbial fermenters and polymer reactors. As analytical solutions of PBE's are available in very few cases, due to the importance of PBE a number of numerical solution methodologies have been proposed to solve the one dimensional PBE (Ramkrishna, 2000, Bove et al., 2005, Ulbert and Lakatos, 2007). In many cases of industrial interest, however, in order to fully characterize the powder in addition to particle size some other particle properties like surface area, chemical composition and crystallinity are needed. These multidimensional problems are very difficult to solve using direct numerical solutions. In modeling suspension polymerization, applying this approach requires solving the PBE describing the droplet size distribution simultaneously with the polymerization reactions occurring inside the droplets. In addition, during the course of process coalescence and brake up of droplets may occur leading to some exchange of species and heat between the droplets what complicates the problem even more. The Monte Carlo (MC) methods are often selected as solution methodology for such complex multidimensional population balance models where direct numerical solution becomes very difficult (Irizarry, 2008, Bárkányi et al, 2011, Zhao and Zheng, 2013).

The aim of the paper is to present a population balance model for batch suspension polymerization of vinyl chloride (VC) which is a complex process of deterministic polymerization reactions inside the monomer droplets and of stochastic discrete event processes of breakage, collisions and coalescence of droplets. A novel MC method is developed and applied for solving the multivariable population balance equation and to analyze the process by simulation.

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2. Model development

2.1 General

Suspension polymerization is used for commercial manufacture of many important polymers including polyvinyl chloride (PVC), polymethyl methacrylate and polystyrene (Caytano Teran and Machado, 2011). PVC is produced by powder polymerization since PVC is insoluble in the VC monomer hence it immediately precipitates out formatting a separate phase.

During the course of polymerization the volume of droplets is changed due to the density difference of monomer and polymer that should be taken into consideration as well. In suspension polymerization of vinyl chloride, however, the volume fraction of the dispersed phase is about 0.3 therefore the total volume of mixture in suspension polymerization can be considered constant.

The dispersed phase is formed by a large population of monomer droplets moving stochastically in the continuous carrier phase of the intensively stirred batch tank reactor. Once the dispersed phase becomes fully developed the tank reactor is heated to the temperature at which the polymerization process is started. Assuming homogeneous temperature distribution over the reactor, subsequently two relevant processes occur in parallel in the reactor. Polymerization reactions (Xie et al, 1991, Kiparissides et al, 1997, Bárkányi et al., 2011) inside the droplets, having rates depending on the actual concentrations and temperature in droplets, form a continuous in time deterministic process. Simultaneously with that, random binary collisions may occur between the droplets moving in the reactor space the frequency of which depends on their number in a unit volume of the reactor, and, despite the stabilizers, collision induced interactions may result in aggregation or only in interchange of some mass of species and heat. Besides, the droplets may suffer break up also due to the shear forces and collisions of eddies. These sequences of events form, in principle, a stochastic discrete event process. In a model of suspension polymerization reactor both processes should be taken into consideration and this can be achieved by using the population balance approach.

2.2 Drop breakage and coalescence rate functions

Breakage and coalescence of monomer droplets are affected by the local mechanical conditions in the dispersion, turbulent energy dissipation and shear forces as well as by such physical properties as the viscosity and density of phases, interfacial tension, and such interfacial phenomena as the surface charge of droplets.

In the past few decades, the drop rate functions given by Coulaglou and Tavlarides (1977) seem to have been the most widely used. In suspension polymerization of vinyl chloride because of the intensive stirring a turbulent flow field is evolved. In the turbulent region, the droplet breakage frequency (1/s) is given as:

$$g(d) = \frac{C_I d^{-2/3} \varepsilon^{1/3}}{1+\phi} \exp\left[-\frac{C_{II} \sigma (1+\phi)^2}{\rho_d d^{5/3} \varepsilon^{2/3}} \right] \tag{1}$$

The binary droplet coalescence rate was given by Tsouris and Tavlarides (1994), with a single adjustable parameter. According to their equation, the collision frequency (m^3/s) can be put in the following form:

$$h(d,d') = \frac{\pi \alpha^{1/2}}{\sqrt[3]{2}} \varepsilon^{1/3} (d+d')^2 \left(d^{2/3} + d'^{2/3} \right)^{1/2} \tag{2}$$

Alopaeus et al. (1999) experienced in their work that this equation gives the collision frequency several orders of magnitude greater than those of Coulaglou and Tavlarides (1977).

Since the coalescence efficiency which provides the ratio of binary collisions of droplets resulting in coalescence is:

$$\lambda(d,d') = \exp\left[-\frac{C_{IV} \mu_c \rho_c \varepsilon}{\sigma^2 (1+\phi)^3} \left(\frac{dd'}{d+d'} \right)^4 \right] \tag{3}$$

the coalescence rate is:

$$F(d,d') = h(d,d') \lambda(d,d') \tag{4}$$

The parameters C_I, C_{II}, C_{IV} and α in Eqs (1-3) were given by Alopaeus et al. (1999). In these equations, d, ε, μ_c, $\rho_{d,c}$, σ, Φ are the droplet diameter (m), energy dissipation rate (m^2/s^3), viscosity of the continuous phase (Pas), average density of the suspension (kg/m^3), interfacial tension (N/m) and volume fraction of dispersed phase, respectively.

2.3 Population balance equation

Consider a large population of interacting monomer drops moving stochastically in the continuous carrier phase of an intensively stirred reactor. The initiator, soluble in the monomer is distributed in the drops also by stirring. 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 drops form a continuous in time deterministic process, while coalescence and breakage of drops with micromixing in the coalescence state form a stochastic discrete event process.

Let υ denote the volume coordinate of drops, $\boldsymbol{c}$ stand for the vector of concentrations of $K\geq 0$ relevant chemical species inside the drops, and T denote the temperature of droplets. Further, let $n(\upsilon,\boldsymbol{c},T,t)$ denote the population density function of the drop population by means of which $n(\upsilon,\boldsymbol{c},T,t)d\upsilon d\boldsymbol{c}dT$ provides the number of drops being in the volume and temperature intervals $(\upsilon,\upsilon+d\upsilon)$ and $(T,T+dT)$ and concentration region $(\boldsymbol{c},\boldsymbol{c}+d\boldsymbol{c})$ at time t in a unit volume of the reactor. Then, taking into consideration the condition that the reactor is perfectly mixed at macro-scale, and for the sake of simplicity, denoting the state of a drop at time t by the vector $(\upsilon,\boldsymbol{c},T)=(\upsilon,\boldsymbol{\chi})$, the meso-scale model of the drop population in the polymerization reactor takes the form

$$\frac{\partial n(\upsilon,\chi,t)}{\partial t}+\nabla_{\chi}\left[\frac{d\chi}{dt}n(\upsilon,\chi,t)\right]=\boldsymbol{M}_{\boldsymbol{c/r}}\left[n(\upsilon,\chi,t)\right]+\boldsymbol{M}_{\boldsymbol{b}}\left[n(\upsilon,\chi,t)\right]+\boldsymbol{M}_{\boldsymbol{a}}\left[n(\upsilon,\chi,t)\right] \tag{5}$$

where the second term on the left hand side of Eq.(5) denotes the rate of change of the population density function (PDF) due to the chemical reactions while the terms on the right hand side of Eq.(5) denote, in turn, the rates of change of the PDF due to collision induce exchange of mass of sepcies, breakage and aggregation of drops. These terms were detailed and analyzed by Lakatos (2011) considering the multi-scale structure of dispersed systems. In this work we present the solution of the PBE (5) using an MC method.

3. Solution by means of a Monte Carlo method

MC methods can be divided into two classes according to the treatment of the time step. These are referred to as “time-driven” and “event-driven” MC (Irizarry, 2008). In time-driven simulations a time step is specified then the simulation implements all possible events within that step. In event-driven, first an event is implemented then the simulation time is advanced by the corresponding value. Here we used an event-driven MC method as follows.

The simulated drop diameter intervals are sectioned to equal parts termed size classes. All droplets are assigned into these classes based on their actual diameters. The collision and breakage processes are modeled as inhomogeneous Poisson processes independent from each other the intensities of which are computed individually for all classes using Eqs (1-4) and their actual number of droplets. Naturally, in the time intervals between subsequent events computations are carried out using homogeneous approximations as it is described as follows.

Initialization: Initial droplet size distribution is generated using the beta distribution and all state variables are given initial value. The number of droplets is *N*. Set the time equal to zero. The simulated drop diameter interval is 1 µm to 250 µm and this interval is sectioned to 25 equal parts.

Step 1: Collision, breakage frequencies and coalescence efficiency are calculated using Eqs (1-4) and the number of droplets in classes. Selection of the next event and event time from all possible events using equations

$$\min_{k}\max_{\Delta t}\left\{P(event\ \#=1)=\left(\lambda_k \Delta t\right)e^{-\lambda_k \Delta t}\right\},\quad k\in\left\{\text{all events}\right\} \tag{6}$$

and

$$\Delta t_k=\frac{1}{\lambda_k} \tag{7}$$

Set the simulation time to: $t_{i+1}=t_i+\Delta t_k$.

Step 2: There is a complex intra-particle dynamics, such as polymerization reactions, so, for all particles integrate the set of intra-particle reactions from t_i to t_{i+1}.

Step 3: If the next event is a *coalescence* one then two droplets are selected randomly from diameter classes d and d'. These droplets are eliminated and a new droplet is formed from these droplets with size $\upsilon_{new} = \upsilon_i + \upsilon_j$. Then set $N:=N-1$. The properties (concentration of initiator and monomer, conversion, moments and so on) of the new droplet are calculated from properties of coalesced droplets.

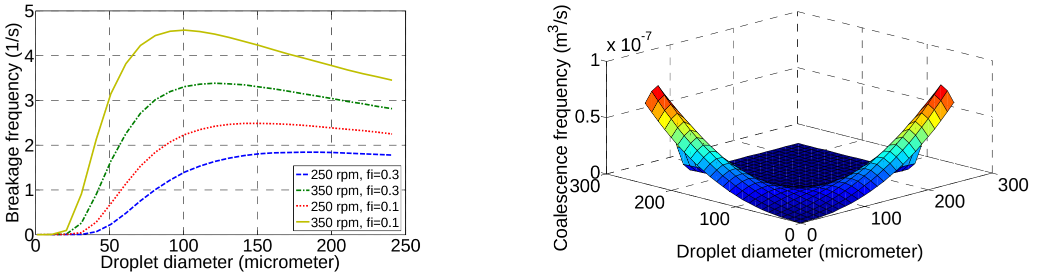
If the next event is a *breakage* one then one droplet is selected randomly from the diameter class d. This droplet is eliminated and two new twin droplets are formed from that $\upsilon_{new} = \upsilon_i / 2$ and set $N:=N+1$. The properties of new droplets are equal with the properties of mother one.

If the next event is a *collision* one then two droplets are selected randomly from diameter class d and d'. There is component transport between droplets but the total number of droplets does not change: $N:=N$. A random number $\omega \in [0,1]$ is generated to calculate the rate of species exchange between the colliding droplets.

Step 4: If $t_{i+1} \geq t_{final}$ then stop, i.e. end the simulation otherwise go to **Step 1**.

4. Results and discussion

The computer program was written and all simulation runs were carried out in MATLAB environment. Eqs (1-3) involve the energy dissipation rate ε which is influenced by the impeller speed, impeller diameter, the power number of impeller and some physical properties of liquid (Nere et al., 2003). In simulation, the dissipation rates 14 m^2/s^3 and 38 m^2/s^3 were used according to two different impeller speeds 250 rpm and 350 rpm assuming volume fractions of dispersed phase *fi*=0.3 and *fi*=0.1.



a

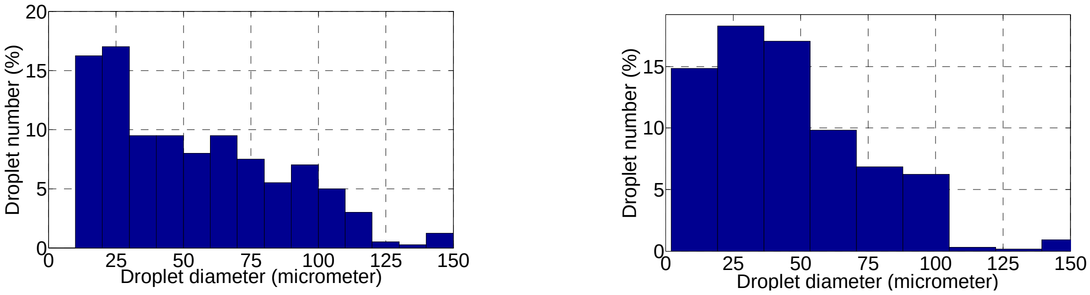
b

Figure 1: a) Influence of droplet diameters on the breakage frequency depending on the impeller speed and volume fraction of dispersed phase; b) Influence of droplet diameters on the coalescence frequency for 350 rpm and fi=0.3.

Figure 1a presents the breakage frequency as a function of droplet diameters depending on the impeller speed and volume fraction of the dispersed phase. The differences are significant. In Figure 1b, the coalescence frequency is presented for the case when the impeller speed is 350 rpm and the volume fraction of dispersed phase is 0.3. Naturally, this surface is symmetrical with respect to the diameters of colliding droplets. The simulation experience has revealed that the effects of impeller speed and volume fraction of dispersed phase on the coalescence frequency are not so conspicuous in this range of droplet diameters therefore the diameter of droplets is the dominant factor.

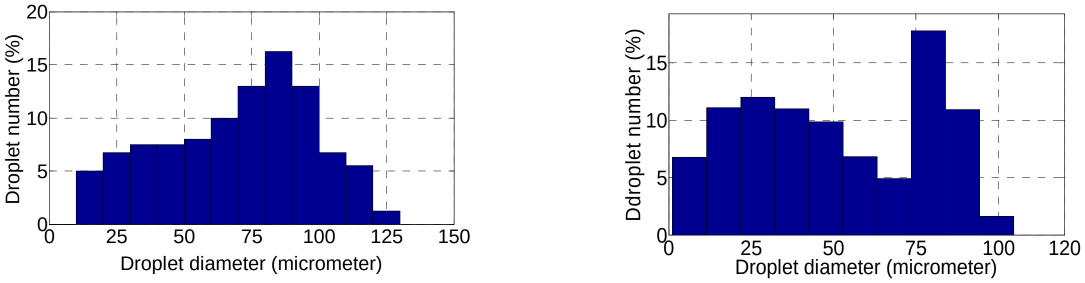
In order to analyze the effects of the initial droplet size distribution and the distribution of initiator on the monomer conversion the breakage and coalescence frequencies (1)-(4) were applied to generate the initial droplet size distribution. In this case, computations were carried out without reactions and the simulation results were compared to the monomer droplet size distributions from the literature published by Zerfa and Brooks (1996a,b). As it is seen in Figure 2 the case when the impeller speed was 350 rpm and the volume fraction of dispersed phase was 0.3 the simulation data fit really well to experimental ones while for the volume fraction 0.1 of dispersed phase the similarity between the experimental and simulation size distribution is not so good.

For simulation of suspension polymerization reactor of vinyl chloride the kinetic data were taken from the literature published by Sidiropoulou and Kiparissides (1990). In order to verify the simulation program test simulation runs were performed with mono-dispersed initial size distribution of monomer droplets under isothermal conditions. The initial distribution of the same amount of initiator in the droplets was also uniform. As a consequence this case provided an ideal reactor mixed perfectly both on macro and micro



a, 350 rpm, *fi*=0.3, experimental data (Zerfa and Brooks, 1996a,b)

b, 350 rpm, *fi*=0.3 (simulation data)



c, 250 rpm, *fi*=0.1, experimental data (Zerfa and Brooks, 1996a,b)

d, 250 rpm, *fi*=0.1 (simulation data)

Figure 2: Comparison of experimental (Zerfa and Brooks, 1996a,b) and simulation data of the initial droplet size distributions

levels and all drops behaved in the system as identical perfectly mixed micro-reactors.

Figure 3a shows the temporal evaluation of monomer conversion. It is seen that the time profile obtained by simulation and the experimental data from the literature (Sidiropoulou and Kiparissides, 1990) run really good with each other. So the computer program was verified for simulating the suspension polymerization of VC under isothermal conditions for 323 K.

To start the simulation first we generated an initial drop size distribution as it seen in Figure 2b. Then we randomly selected the drops which contained initiator at the beginning of the process. The total amount the initiator distributed in the monomer droplets was the same in all cases (0.29% on moles of monomer), and the simulation runs were carried out in accordance with the procedure described in Section 3. Note that starting simulation of the polymerization process from the initial size distribution of droplets shown in Figure 2b the temporal variation of the number of droplets resulted in random events of breakage and coalescence became stabilized by the side of some fluctuations.

Figure 3b presents the temporal evaluations of monomer conversion as a function of the initial distribution of the initiator. The results demonstrate well that the differences in distribution of the initiator may affect the average monomer conversion significantly. If only less than 75 % of droplets contain initiator initially the monomer conversion is significantly lower compared with the ideal case when initially all droplets contain initiator. On the basis of these results and according to the actual performances of the VC polymerization reactors, it is strongly advisable to operate the reactors in the region of satisfactory macro- and micro-mixing states that can ensure at least 75 % initiator distribution within the dispersed phase.

5. Conclusion

A novel Monte Carlo method was presented for solution of the population balance equation of suspension polymerization of vinyl chloride. The simulation results of initial drop size distribution and monomer conversion proved to be in good agreement with the experimental data from literature. So we can say that this method of modeling can describe the phenomena in suspension polymerization of VC properly. The effects of heat transfer and the inhomogeneity of temperature both in the droplets and the reactor are the subject of a further study.

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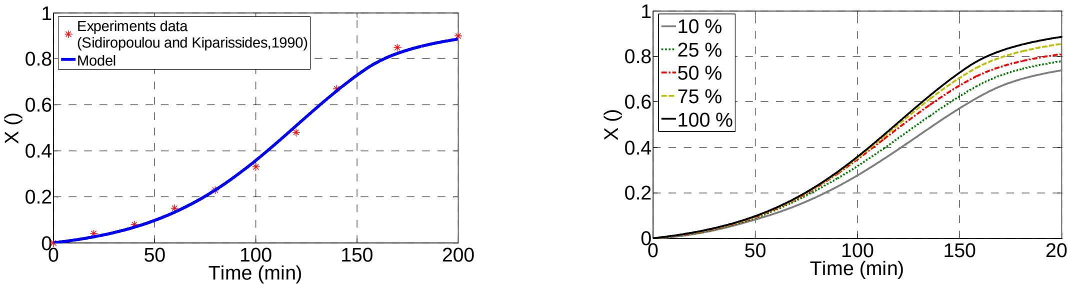

a

b

Figure 3: a) Results of parameter identification of the polymerization reaction model; b) Temporal evolution of the monomer conversion as a function of the initial distribution of initiator in the droplets

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