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RESEARCH ARTICLE

Modelling of heat exchange between drops in suspension polymerization of vinyl chloride

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Abstract

A population balance model is presented for suspension polymerization of vinyl chloride in a batch reactor to investigate the thermal properties of the system. Reactions are described using a simplified reaction model focusing on the heat generation of the highly exothermic polymerization reactions. The temperature of the continuous phase is assumed to be homogeneous over the reactor and the effects of some temperature rise of droplets due to the exothermic polymerization reactions and the possible heat exchange because of the coalescence/redispersion process are analysed. The population balance equation is solved applying a Monte Carlo method by coupling the deterministic polymerization reactions inside the droplets with the discrete event process induced by collisions of droplets.

The results obtained by simulation show that rise in the temperature of droplets over the mean temperature of continuous phase lead to acceleration of the process. The possible size distribution of droplets and no smooth distribution of the initiator in those decrease the process efficiency.

Keywords

Suspension polymerization · vinyl chloride · population balance model · collisional heat exchange · Monte Carlo method

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Introduction

Suspension polymerization is used for commercial manufacture of many important polymers including polyvinyl chloride (PVC), polymethyl methacrylate and polystyrene. In this process, two immiscible liquids are mixed to produce a dispersion of monomer droplets in a continuous aqueous phase. The initiator is dissolved in the monomer droplets where the polymerization reactions occur.

Both the size and size distribution of the droplets in the agitated dispersion depend on the extent of droplet breakup and coalescence which, in turn, depend on the type and concentrations of suspending agents and on the volume fraction of the dispersed phase [1, 2]. Droplet stability is also influenced by coalescence. The most commonly used suspending agents for vinyl chloride suspension polymerization are water-soluble polymers such as hydroxylpropyl methylcellulose (HPMC) and partially hydrolysed polyvinyl acetate, commonly called PVA [3]. The adsorption of such molecules at the monomer-water interface reduces the interfacial tension and hence reduces the energy required to form droplets. Droplet stability depends largely on the nature of the droplet stabilizer. If no stabilizers are used to protect the droplets, the suspension would be unstable and the final polymer particles would reach an undesirable size.

The droplet size distribution and its temporal evolution can be described by applying the population balance approach [4]. In modelling suspension polymerization, however, applying this approach requires solving the population balance equation (PBE), simultaneously with computing the polymerization reactions going on inside the droplets. In addition, during the course of collisions of droplets coalescence and breakup as well as some interchange of chemical compounds and heat, termed micromixing by coalescence/ redispersion events, may occur what complicates the problem even more. As analytical solutions of PBEs are available in very few cases, numerical techniques are essential in most practical applications. There are several numerical methods available that satisfy the accuracy requirements [5] but, taking into consideration the random nature of breakage, coalescence and micromixing processes Monte Carlo (MC) simulation also seems to be a suitable method for solving this numerical problem.

Recently, Bárkányi et al. [6] and Bárkányi et al. [7, 8] have analysed the suspension polymerization process of vinyl chloride in batch reactors applying an MC method taking into account breakage and coalescence of droplets, as well as micromixing of species induced by collisions. Binary breakage into two equal volumes, binary coalescence and randomly varying mass exchange between the colliding droplets were considered under isothermal conditions.

The aim of the present paper is to model and analyse a suspension polymerization process of vinyl chloride in which beside the polymerization reactions inside the droplets only collision induced heat exchange occurs between the colliding droplets. It is assumed that stabilization of monomer droplets is perfect therefore no coalescence, breakage or mass exchange take place in the reactor studying in this way some thermal aspects of the process. The kinetic data of vinyl chloride polymerization are taken from the literature [9, 10].

Model development

General

Suspension polymerization usually is carried out in batch reactors. PVC is produced by powder polymerization since PVC is insoluble in the vinyl chloride monomer (VCM) hence it immediately precipitates out formatting a separate phase. In suspension polymerization of VCM the free radical polymerization reactions take place in the monomer droplets because the initiator is dissolved in those.

Suspension polymerization exhibits some advantages over the other polymerization processes: bulk, solution and emulsion polymerization [11]. Indeed, suspension polymerization is characterized by favourable thermal conditions but the advantages are not restricted to good temperature controlling. Coagulation is largely confined to the droplet interiors and coalescence of polymerizing droplets can be restricted. That is why suspension polymerization is used for the large scale production of PVC. In that case, the initial droplet diameters, and the final particle sizes, range between 10 μm and 100 μm [12].

The properties of PVC are influenced by the polymerization conditions: reactor temperature, stirring conditions, reactor size and concentration of initiator. The temperature of polymerization is one of the most important parameters. Only 1 or 2 K differences in temperature can induce significant changes in the properties of polymer products.

As the dispersed phase, formed by a large population of monomer droplets moving stochastically in the continuous carrier phase of the intensively stirred batch reactor becomes fully developed the reactor is heated to the temperature at which the polymerization process is started. Assuming homogeneous temperature distribution over the continuous phase of the reactor, subsequently two relevant processes are going on parallel in the reactor. The highly exothermic polymerization reactions [6] inside the droplets, having rates depending on the actual concentrations and temperature, 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 the size and number of droplets in a unit volume of the reactor. Assuming perfect stabilization, coalescence and breakage of droplets becomes negligible. Besides, taking into account that the rate of diffusional mass transfer is smaller with some orders of magnitude than that of heat it is justified to assume that collisions of droplets, next termed collision/redispersion events, induce only some heat exchange between the colliding droplets, caused by their possible temperature differences, with negligible species mass interactions. This sequence of events forms, in principle, a stochastic discrete event process. In a model of suspension polymerization reactor both processes, i.e. the deterministic polymerization reactions and the discrete event process of direct heat transfer between the colliding droplets should be taken into consideration and this can be achieved by using the population balance approach.

During the course of polymerization the volume of droplets is also changed due to the density difference of monomer and polymer that should be taken into account 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.

Polymerization reactions

From a kinetic point of view, polymerization of VCM is considered to take place in three stages [13].

Stage 1. During the first stage, primary radicals formed by the thermal fragmentation of initiator rapidly react with monomer molecules to produce PVC macromolecules which are insoluble in the monomer phase. The reaction mixture consists mainly of pure monomer, since the polymer concentration is less than its solubility limit (monomer conversion ($X < 0.1\%$).

Stage 2. This stage extends from the time of appearance of the separate polymer phase to a fractional conversion Xf at which the separate monomer phase disappears ($0.1\% < X < Xf$). The reaction mixture consists of four phases, namely, the monomer-rich phase, the polymer-rich phase, the aqueous phase, and the gaseous phase. The reaction takes place in the monomer and polymer phases at different rates and is accompanied by transfer of monomer from the monomer phase to the polymer one so that the latter is kept saturated with monomer. The disappearance of the monomer phase is associated with a pressure drop in the reactor.

Stage 3. Finally, at higher conversions ($X > Xf$) only the polymer-rich phase swollen with monomer exists. The monomer mass fraction in the polymer phase decreases as the total monomer conversion approaches a final limiting value [13].

The reactions accounting for the vinyl chloride suspension polymerization are summarized in Table 1, where I denotes the initiator, I^* is the active initiator radical, k_d denotes the initiator decomposition rate coefficient [1/sec], k_p is the propagation rate coefficient [m^3/(mol•sec)], k_t stands for the rate coefficient of termination [m^3/(mol•sec)], k_{tM} is the chain transfer rate coefficient [m^3/(mol•sec)], M denotes the monomer, R_i is the growing polymer chain with chain length i, and P_i is the closed polymer chain with chain length i.

When analysing the properties of the polymer product beside tracking the changes of concentrations of the initiator and monomer it is reasonable to compute also the first three leading moments of the live and dead polymer chains. This formulation requires 8 variables and 8 differential equations and provides a sufficiently detailed description of the polymerization reactions [6–8]. However, here we focus our attention on modelling the thermal effects of the system, and since the propagation step is the most important one in determining heat of polymerization the behaviour of droplets can be described simply by the mass balances of initiator, monomer and growing polymer chains together with the energy balance [14].

Denoting the finite total concentration of the infinite number of live polymer radicals as

$$\nu_0 = \sum_{i=0}^{\infty} P_i \tag{1}$$

the following balance equations are described for each monomer droplet.

Mass balance for initiator:

$$\frac{d(\upsilon c_I)}{dt} = -k_d c_I \tag{2}$$

Mass balance for monomer:

$$\frac{d(\upsilon c_M)}{dt} = -(2 f k_d c_I c_M + k_p c_M \nu_0 + k_{tM} c_M \nu_0) \tag{3}$$

Mass balance for live polymer radicals:

$$\frac{d(\upsilon \nu_0)}{dt} = 2 f k_d c_I - k_t \nu_0^2 \tag{4}$$

From Eq. (3) the monomer conversion is computed as

$$\frac{dX}{dt} = -\frac{d(\upsilon c_M)}{dt}\frac{M_w}{m_0} \tag{5}$$

and the balance of droplet volume takes the form

$$\frac{d\upsilon}{dt} = \frac{d\upsilon_P}{dt} + \frac{d\upsilon_M}{dt} \tag{6}$$

Applying the Quasi-Steady-State Assumption (QSSA) for to the growing polymer chains, Eq. (4) become:

$$\nu_0 = \sqrt{\frac{2 f k_d c_I}{k_t}} \tag{7}$$

Energy balance for a droplet:

$$\frac{\rho c_p d(\upsilon T)}{dt} = \dot{Q}_{reaction} + \dot{Q}_{transfer} \tag{8}$$

In Eqs. (2)-(8) υ is the droplet volume, c_I denotes the concentration of initiator in a droplet, c_M is the concentration of monomer, T is the temperature of droplet, c_p denotes the heat capacity of droplet, ρ denotes its density, $\dot{Q}_{reaction}$ represents the heat produced by exothermic polymerization reactions and $\dot{Q}_{transfer}$ is the heat removed to the continuous phase.

The 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. Bimolecular termination reactions between chain radicals become diffusion controlled at high polymer concentrations or high conversion leading to an initial increase in the polymerization rate and molecular weight. This condition is known as the gel effect or Trommsdorff effect. Typically the termination rate coefficients are affected first by the gel effect because they involve diffusion of two bulky polymer radicals. The diffusional limitation is usually modelled by multiplying the low conversion reaction rate coefficients (k_0) by a gel effect factor (GF) that decreases with increasing conversion [12]. Hence the effective rate coefficient for a reaction is given by:

$$k_{eff} = k_0 \cdot GF \tag{9}$$

The most commonly used gel effect correlation is:

$$GF = \frac{a_1}{1 + a_2 \cdot X_f^{a_3}} \tag{10}$$

We can use this correlation simply by specifying the correlation parameters (a_1, a_2 and a_3).

During the course of simulation, the mass balances of the initiator and monomer, as well as the zero moment balance were computed. Therefore, in the next sections the vector of concentrations $\boldsymbol{c}$=(c_1,c_2,c_3,) denotes, in turn, the concentrations of initiator, monomer, and the zero moment of the live polymer chains.

Population balance model

Let now υ denote the volume of a droplet, $\boldsymbol{c}$ stand for the vector of concentrations of K=3 relevant chemical species inside the droplets, and let T denote the droplet temperature. Then, assuming that the reactor is perfectly mixed at macro-scale and the motion of droplets in the continuous carrier phase is fully stochastic without orientation the micro-scale state of a droplet, in general case, is given by the vector $(\upsilon, \mathbf{c}, T) \in \mathbf{R}^{K+2}$ without indicating its position and velocity in the space of the reactor [15]. Then, during the course of the process, this state vector is changed due to the following relevant micro-scale interactions:

The concentrations of chemical species are changed continuously in time because of the polymerization reactions. This is a deterministic, time continuous process thus concentrations in a droplet are governed by the set of differential equations

$$\frac{d\mathbf{c}\,(t)}{dt} = \mathbf{R}_r\left[\mathbf{c}\,(t)\,, T\,(t)\right] \tag{11}$$

which is formed by Eqs (2)-(4). Here, $\mathbf{c} = (c_1, c_2, c_3)^T$ and $(.)^T$ denotes the transposition operation.

Tab. 1. Free-radical polymerization reactions of vinyl chloride

Decomposition of the initiator:	$I \xrightarrow{k_d} 2I^*$		
Chain initiation:	$I^* + M \xrightarrow{k_d} R_1$		
Propagation:	$R_1 + M \xrightarrow{k_p} R_2$		$R_i + M \xrightarrow{k_p} R_{i+1}$
Chain transfer:	$R_1 + M \xrightarrow{k_{tM}} R_1 + P_1$		$R_i + M \xrightarrow{k_{tM}} R_i + P_i$
Termination:	$R_i \xrightarrow{k_t} P_i$	$R_i + R_j \xrightarrow{k_{tc}} P_{i+j}$	$R_i + R_j \xrightarrow{k_{td}} P_i + P_j$

The volume of droplets is also changed continuously in time because of polymerization reactions and significant difference between the densities of monomer and polymer. The volume of a droplet is governed by a simple differential equation

$$\frac{d\upsilon(t)}{dt} = f_\upsilon\left[\mathbf{R}_r\left(\mathbf{c}(t), T(t)\right)\right] \tag{12}$$

which consists of the terms given in Eq.(6).

Because of generation of heat by the exothermic polymerization reactions and heat transfer between the continuous phase and droplets, the temperature of a droplet is varied in time continuously. However, to this deterministic, time continuous process the discrete in time process of collision induced interchanges of heat is superimposed, since collisions of droplets are going on randomly. It is assumed that these coalescence/redispersion events may induce jump-like changes of temperatures in the colliding droplets because of their possibly different temperatures the extents of which, depending on the actual collision conditions are also random characterized by a parameter $\omega \in [0, 1]$ as it was determined in the case of collision induced heat transfer of solid particles in gas-solid systems [16, 17].

$$\omega = 1 - \exp\left[-h_{c/r}a_{c/r}\theta_{c/r}\left(\frac{m_i c_{pi} + m_j c_{pj}}{m_j c_{pj} m_i c_{pi}}\right)\right] \tag{13}$$

where c_{pi} and c_{pj} are the heat capacities and m_i and m_j are the masses of colliding droplets.

In Eq. (13) $h_{c/r}$, $a_{c/r}$ and $\theta_{c/r}$ denote, respectively, the heat transfer coefficient, contact surface and contact time between the droplets in a coalescence/redispersion event. Since these quantities appear to be random the variable ω is also random taking values from the closed interval [0,1]. The value $\omega = 0$ means no heat exchange during the collisions while the value $\omega = 1$ denotes such case when total equalization of temperatures of the colliding droplets occurs. As a consequence, the temperature of a droplet is governed by the stochastic differential equation

$$dT(t) = f_T\left[\mathbf{R}_r\left(\mathbf{c}(t), T(t)\right)\right]dt - ha\left[T(t) - T_f\right] + \int_V \psi_{c/r}(\omega, T)\mathrm{N}(\upsilon, dt) \tag{14}$$

where the terms on the right hand side describe, in turn, the rate of change of temperature due to polymerization reactions, the droplet-continuous phase heat transfer and jump-like changes by the coalescence/redispersion events. Here, h denotes the droplet-continuous phase heat transfer coefficient, a is the droplet surface, T_f denotes the continuous phase temperature, function $\psi_{c/r}$ provides the temperature jump induced by a coalescence/redispersion event and characterized by the random parameter ω, and N denotes a Poisson process counting these random events in the volume V of suspension depending on the volumes of droplets.

The set of differential equations (11)-(14) describes the behaviour of droplets entirely by tracking the time evolution of the state of each droplet individually. However, the complexity of this mathematical model does not allow overcoming the computational complexity related to the system of Eqs. (11)-(14). Instead of following the evolution of each single droplet it is reasonable to consider the collective description of those utilising their statistical similarities and defining an appropriate mesoscopic length-scale between the micro- and macro-scales [15].

Defining the population density function given as a mapping $(\upsilon,\boldsymbol{c},T,t) \rightarrow n(\upsilon,\boldsymbol{c},T,t)$ by means of which $n(\upsilon,\boldsymbol{c},T,t)d\upsilon d\boldsymbol{c}dT$ provides the number of droplets being in the volume $(\upsilon,\upsilon+d\upsilon)$ and temperature $(T,T+dT)$ intervals and concentration region $(\boldsymbol{c},\boldsymbol{c}+d\boldsymbol{c})$ at time $t$in a unit volume of the reactor. Then the population balance equation takes the form

$$\frac{\partial n(\upsilon,\mathbf{c},T,t)}{\partial t} + \frac{\partial}{\partial\upsilon}\left[\frac{d\upsilon}{dt}n(\upsilon,\mathbf{c},T,t)\right] + \frac{\partial}{\partial\mathbf{c}}\left[\frac{d\mathbf{c}}{dt}n(\upsilon,\mathbf{c},T,t)\right] + \\ +\frac{\partial}{\partial T}\left[\frac{dT}{dt}n(\upsilon,\mathbf{c},T,t)\right] = M_{c/r}\left[n(\upsilon,\mathbf{c},T,t)\right] \tag{15}$$

where on the left hand side are the rates of change of the population density function because of the deterministic continuous processes while the operation $M_{c/r}$ on the right hand side represents the collision-induced process which takes the form [16, 17]

$$M_{c/r}\left[n(\upsilon,\mathbf{c},T,t)\right] = -S_{c/r}n(\upsilon,\mathbf{c},T,t) + \\ \int_0^1 \frac{2S_{c/r}}{p_\upsilon\omega N(t)}\int_{T_{\min}}^{T_{\max}} n\left[\upsilon,\mathbf{c},\left(\frac{2(T-y)}{p_\upsilon\omega}+y\right)\right]n(\upsilon,\mathbf{c},y,t)\,f_\omega(\omega)dyd\omega \tag{16}$$

where $\omega \in [0, 1]$ is the random number characterizing the extent of equalization of temperatures with probability density function f_ω, $p_\upsilon = \upsilon'/(\upsilon+\upsilon')$ and N denotes the total number of droplets. Function $S_{c/r}$ provides the frequency of binary collisions of droplets of volumes υ and υ' resulting in exchange of heat induced by a coalescence/redispersion event. The first and second terms on the right hand side of Eq.(19) describe, respectively, the rates of decrease and increase of the number of droplets of state (υ,$\mathbf{c}$,T) caused by these events.

Eqs. (15)-(16) is the meso-scale model of the droplet population in suspension polymerization reactor and, since in this process there are no mass transfer interactions between the dispersed and continuous phases, and the temperature over the continuous phase of reactor is assumed to be homogeneous, Eq. (15) provides, in principle, the model of the whole reactor as well.

Note, that the macro-scale model can be formulated by means of the joint moments of volume, concentrations and temperature variables defined as

$$\mu_{k,l_1,l_2...l_K,m}(t) = \int\limits_{T_{\min}}^{T_{\max}} \int\limits_{\mathbf{c}_{\min}}^{\mathbf{c}_{\max}} \int\limits_{0}^{\upsilon_{\max}} \upsilon^k c_1^{l_1} c_2^{l_2} ... c_K^{l_K} T^m n(\upsilon, \mathbf{c}, T, t)\, d\upsilon d\mathbf{c} dT,$$

$$k, l_1, l_2 ... l_K, m = 0, 1, 2... \quad (17)$$

by means of which the mean temperature of droplet population over the reactor is expressed as

$$\langle T \rangle (t) = \frac{1}{\mu_{0,0,0...0,0}(t)} \int\limits_{T_{\min}}^{T_{\max}} \int\limits_{\mathbf{c}_{\min}}^{\mathbf{c}_{\max}} \int\limits_{0}^{\upsilon_{\max}} T n(\upsilon, \mathbf{c}, T, t)\, d\upsilon d\mathbf{c} dT \quad (18)$$

while the mean concentration of the k^{th} species over the reactor can be expressed as

$$\langle c_k \rangle (t) = \frac{1}{\mu_{0,0,0...0,0}(t)} \int\limits_{T_{\min}}^{T_{\max}} \int\limits_{\mathbf{c}_{\min}}^{\mathbf{c}_{\max}} \int\limits_{0}^{\upsilon_{\max}} c_k n(\upsilon, \mathbf{c}, T, t)\, d\upsilon d\mathbf{c} dT,$$

$$k = 1, 2, 3 \quad (19)$$

The numerical solution of the multidimensional population balance equation (15) seems to be a crucial problem thus making use of the randomness of the collision induced processes, it was solve by using the Monte Carlo method.

Solution by means of the Monte Carlo method

In this work we used a “time-driven” MC method. In time-driven simulations a time step is specified then the simulation implements all possible events within that step [18]. The used MC algorithm is described in this section. It is based on generating random numbers from uniform probability distribution in (0,1). Fig. 1 represents the scheme of Monte Carlo method used during simulation; the steps of this method are the following:

Initialization: Initial droplet size distribution is generated and all state variables are given initial value. Number of droplets is N. Set the time equal to zero.

Step 1: Next event time. The next event time will be after time *dt*.

Set time to: $t = t + dt$.

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-dt* to *t*. In this step the volume balance of droplets, the mass balance of initiator and monomer, as well as the zero moment of live polymer chains are calculated.

Step 3: The collision takes place. Two droplets are selected randomly which collide with each other, but the volumes of droplets are not changed in the collision. There is only heat transport between droplets. A random number is generated to calculate the rate of heat exchange between the colliding droplets.

The heat transfer between two colliding droplets was calculated using the following equations

$$T_i = T_{i0} + \frac{c_{p_j} m_j}{c_{p_i} m_i + c_{p_j} m_j} \omega \left(T_{j0} - T_{i0} \right), \quad 0 \le \omega \le 1 \qquad (20)$$

$$T_j = T_{j0} - \frac{c_{p_i} m_i}{c_{p_i} m_i + c_{p_j} m_j} \omega \left(T_{j0} - T_{i0} \right), \quad 0 \le \omega \le 1 \qquad (21)$$

where T_{j0} and T_{i0} denote the temperatures of droplets before collision. Here, the parameter ω was computed using a uniform probability distribution in (0,1).

Step 4: If the final time is reached, end the simulation; otherwise go to step 1.

Results and discussion

The corresponding computer program and all simulation runs were written and carried out in MATLAB environment.

In the first step the simulation program was identified. During the simulation we calculated the gel effect using Eqs (8) and (9). The three parameters of gel effect were defined and the results were compared with measurement data [9]. The simulation and literature data run really good with each other [8].

Some preliminary simulations were carried out in which the effect of the total number of elements was analysed. These simulation runs revealed that a thousand element droplet population proved to be sufficient to simulate the process with reliable approximation [8].

Accordingly in simulation runs a thousand-element droplet population was used examining the effects of micromixing processes on the mean monomer conversion. During the course of simulation perfect stabilization of droplets and negligible component transport were assumed so that only heat transport occurred between the colliding droplets. In our previous work the component transport was analysed without heat transport [6].

The aim of this simulation was to show the effects of the heat generated in exothermic polymerization reactions. In all cases it was assumed that the temperature of the continuous phase was constant and the temperature of droplets was calculated in all time steps. The influence of the heat exchange between the droplets has been studied by observing the mean value of conversion summarized over all droplets participating in the suspension polymerization process of VC.

Short description of simulations:

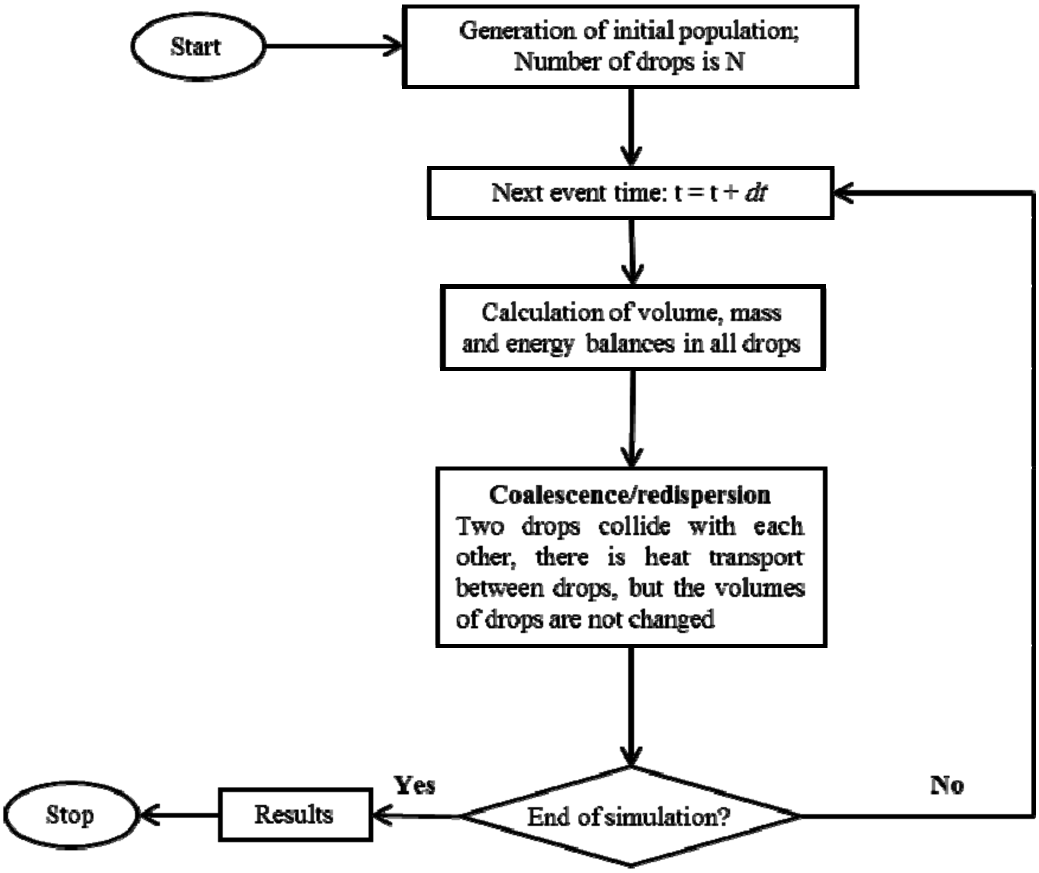

Fig. 1. The scheme of Monte Carlo method used in simulation

- The droplets were mono-dispersed; initially all droplets contained the same amount of initiator; the reaction conditions were isothermal.
- The droplets were mono-dispersed; the droplets contained different amounts of initiator; the reaction conditions were non-isothermal.
- The droplets were dispersed with an initial droplet size distribution; all droplets contained proportionally the same amount of initiator; the reaction conditions were isothermal.
- The droplets were dispersed with an initial droplet size distribution; all droplets contained proportionally the same amount of initiator; the reaction conditions were non-isothermal.

First we computed the monomer conversion when initially all droplets contained the same amounts of initiator and the diameters of droplets were equal. Fig. 2 represents the cases when the reactor was isothermal, the temperature of the continuous phase was homogeneous over the reactor and it was able to distract the heat generated by reactions in droplets. In Fig. 2 the curves (- -) and (· ·) show evolutions of the mean monomer conversion when those were computed allowing maximum 1 K and 5 K differences between the temperatures of droplets and that of the continuous phase. In these cases, the heat transfer coefficients were defined so that the rise in temperature of droplets might achieve maximum 1 K (- -) and (· ·) 5 K.

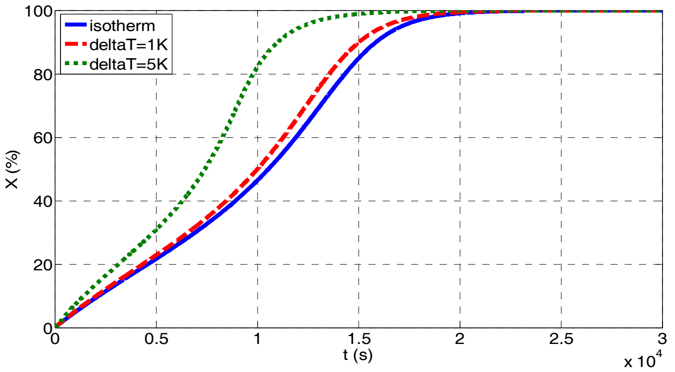

Fig. 2. Evolution in time of the monomer conversion if initially all droplets contained the same amounts of initiator

In Fig. 3 we can see the mean temperature of droplets over the reactor. Jumps in temperature are seen in both cases between 10000 and 12000 seconds, respectively. If we look at Fig. 2 than we can see that the monomer conversion reaches the critical conversion (~75%) at this time. The polymerization rate peaks at critical conversion and decreases drastically after that. This peak in polymerization rate will result in large temperature increase in the reactor [19]. We can say that the effect of temperature of droplets is significant. In the next cases the maximum rise in temperature was 1 K, because the effect of temperature on the quality of final product may be significant.

In the next simulation runs all droplets contained initiator but not the same amounts. The initiator was distributed between the

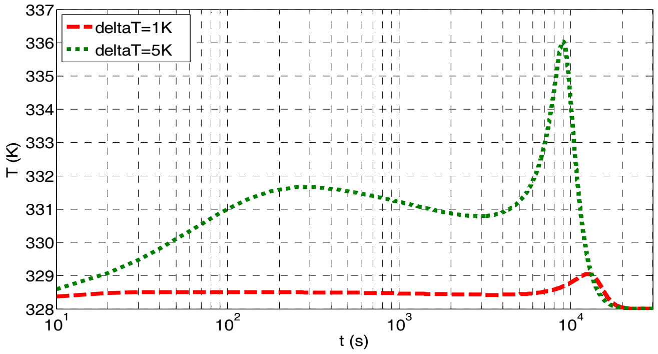

Fig. 3. Evolution in time of the mean temperature of droplets

droplets in small random units. These small units were:

$$ni_0 = b(ni/1000) \tag{22}$$

$$ni_0 = b(ni/10000) \tag{23}$$

where *ni* is the total amount of initiator in the system and *b* is a uniformly distributed random number between 0 and 1.

In Fig. 4 we can see the effects of the initial distribution of initiator on the mean monomer conversion. In these simulation runs the reactor was kept isothermal. It is seen in Fig. 4 that the effects of the initial distribution of the initiator in droplets on the process may be significant.

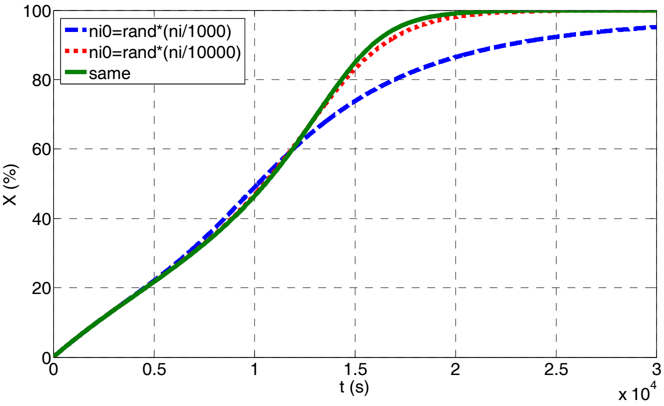

Fig. 4. Evolution in time of the monomer conversion when the initiator was initially distributed randomly in the droplets

In Fig. 4 the monomer conversion drawn by lines (· ·; - -) is compared to the case when initially all droplets contained the same amount of initiator (-). The maximum and minimum values of initiator at the start of polymerization are presented in Table 2. The smaller is ni_0 the smaller is the difference between c_{Imin} and c_{Imax} in droplets at the beginning of the process. The effects of the distribution of initiator are negligible if ni_0 is properly small.

In the previous cases, we studied the effects of temperature and of the initial distribution of initiator in the droplets on the mean monomer conversion separately. Next, we analysed the collective effect of both parameters on the mean monomer conversion. Since in these cases droplets of the same diameter value contained different amounts of initiator the reaction rates in the droplets were not the same which resulted in temperature differences of droplets. Then, the effects of partial or total equalization of temperatures of the colliding droplets during the coalescence/redispersion events were investigated.

Tab. 2. The maximum and minimum values of initiator initially

Case	c_{Imin} (mol/m^3)	c_{Imax} (mol/m^3)
(-)	2.7024	2.7024
(- -)	0.6811	5.8294
(· ·)	1.8657	3.4846

Fig. 5 (**- -**) presents the results of simulation for parameters $ni_0=b(ni/1000)$, $\Delta T = 1$ K and when there was total heat exchange between droplets which collided. It is compared to the case when initially all droplets contained the same amount of initiator and $\Delta T = 1$ K (· ·). The line (-) represents the case when it was $ni_0=b(ni/1000)$ but the reactor was isothermal.

Fig. 6 (**- -**) presents the case for $ni_0=b(ni/10000)$, $\Delta T = 1$ K and when there was total heat exchange between droplets which collided. It is compared to the case when initially all droplets contained the same amount of initiator and $\Delta T = 1$ K (· ·). The line (-) represents the case when it was $ni_0=b(ni/10000)$ but the reactor was was isothermal. Figs. 5 and 6 illustrate well that the monomer conversion reached its final value earlier when initially all droplets contained the same amounts of initiator (· ·).

In all previous cases, the heat exchange between the colliding droplets was total. Next, we analysed the effects of partial heat exchange between droplets. The conditions were the same, namely the initiator was distributed in small random units and all droplets contained some initiator at the start. In these cases, as those are shown in Figs. 7 and 8 the two curves run with each other so weather total or partial heat exchange occurs in a coalescence/redispersion is not relevant. This is because the maximum allowed rise of temperature in droplets during polymerization was 1 K and all droplets contained initiator at the start of the process the temperature differences of droplets have proved not high enough to produce significant effects by this heat exchange.

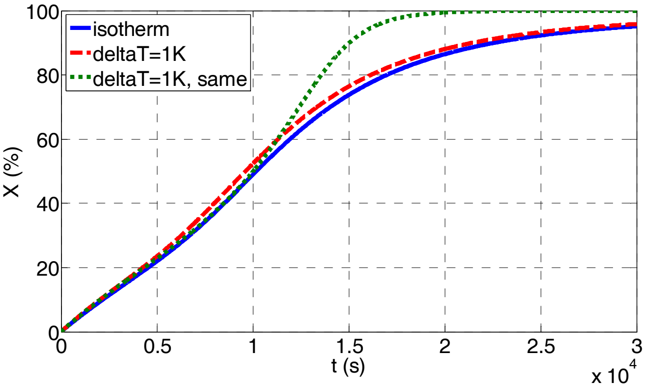

Fig. 5. Evolution in time of the monomer conversion $ni_0=b(ni/1000)$

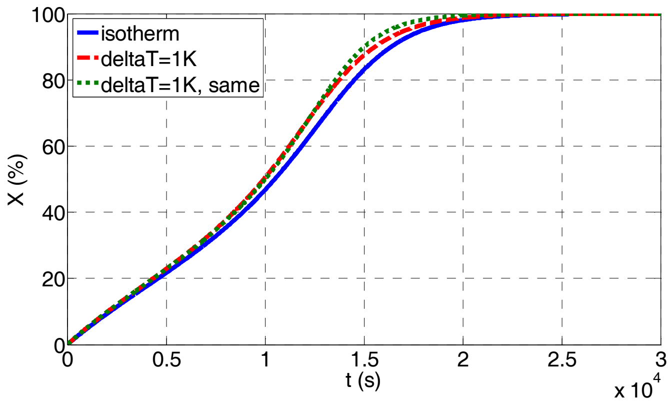

Fig. 6. Evolution in time of the monomer conversion ni_0=*b(ni/10000)*

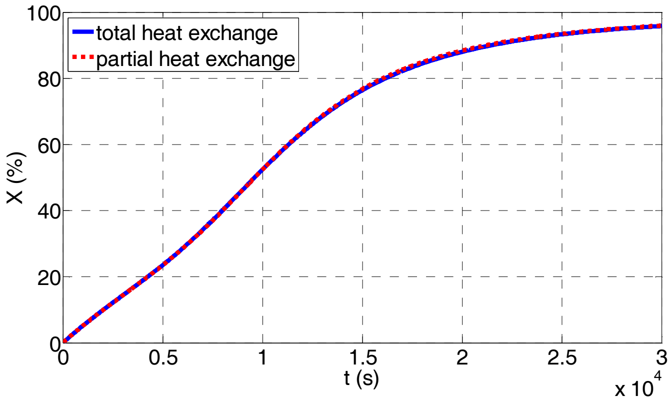

Fig. 7. Evolution in time of the monomer conversion ni_0=*b(ni/1000)*

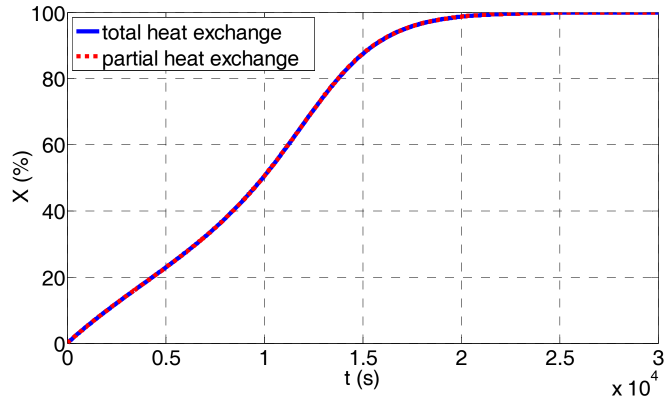

Fig. 8. Evolution in time of the monomer conversion ni_0 =*b(ni/10000)*

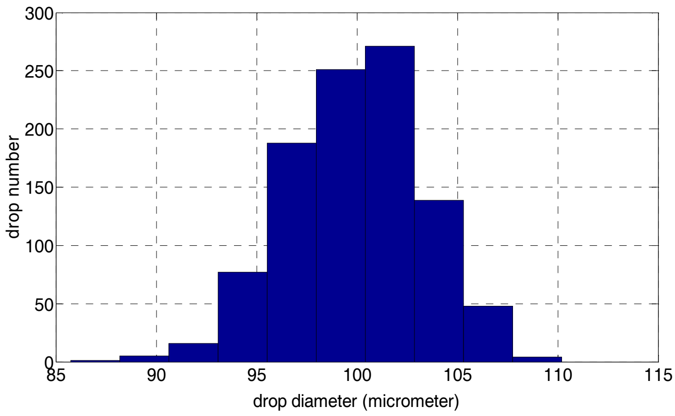

Fig. 9. Initial droplet distribution

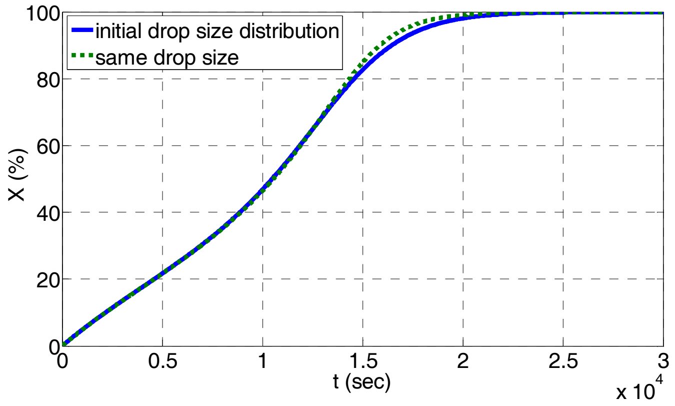

Fig. 10. Influence of the initial droplet size distribution on evolution in time of the monomer conversion

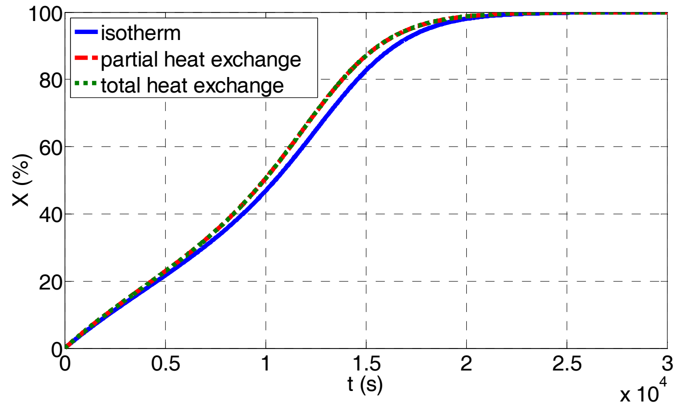

Fig. 11. Effects of the heat exchange between the colliding droplets on evolution of monomer conversion compared with the case of homogeneous reactor temperature

Finally, the effects of the initial droplet size distribution were analysed by generating an initial size distribution using normally distributed pseudorandom numbers. A typical droplet size distribution is seen in Fig. 9.

First we analysed the effect of the initial droplet size distribution. Since the droplet sizes were in a relatively tight size range the effect of this parameter has proved not significant although we can see in Fig. 10 that even this tight size range caused some difference in the mean monomer conversion. The mean monomer conversion reached the final value slower when the initial droplet size distribution was as shown in Fig. 9 compared with the case when it was mono-dispersed.

Fig. 11 shows evolutions of the monomer conversion when partial and total heat exchange occurred between the colliding droplets compared with the case when the temperature in the reactor was totally homogeneous. The same initial droplet size distribution was assumed in each run. Again, it is seen the curves of partial heat exchange (- -) and total heat exchange (· ·) run together.

Conclusions

A population balance model was presented for suspension polymerization of vinyl chloride in a batch polymerization reactor. The stabilization of droplets was assumed to be perfect so there was not any component transport between the continuous phase and droplets as well as between the droplets during their collisions. The temperature of the continuous phase was assumed to be homogeneous over the reactor and the effects of the temperature rise of droplets due to the exothermic polymerization reactions and the possible heat exchange because of the coalescence/redispersion were analysed.. The resulted population balance equation was solved by using a Monte Carlo method by coupling the deterministic polymerization reactions with the discrete event process induced by collisions of droplets.

The results obtained by simulation showed that allowing maximum 5 K rise in the temperature of droplets over the mean temperature of continuous phase led to significant acceleration of the process. The size distribution of droplets and no smooth distribution of the initiator in those decreased the efficiency of the process. When the temperature rise of droplets over the mean temperature of continuous phase was small, i.e. maximum 1 K then the influence of the heat exchange between the colliding droplets on the process proved to be negligible.

Notation

a	droplet surface
$a_{1,2,3}$	parameters
$a_{c/r}$	contact surface between the droplets in a coalescence/redispersion event
$\mathbf{c}$	vector of concentration variables in a droplet
c_I	concentration of initiator in a droplet [mol/ m^3]
c_M	concentration of monomer in a droplet [mol/ m^3]
c_p	heat capacity of droplet [J/mol•K]
f	factor
f_ω	probability density function
I	concentration of initiator [mol/ m^3]
k_0	low conversion reaction rate coefficients [m^3/(mol•s)]
k_d	initiator decomposition rate coefficient [1/s]
k_{eff}	effective rate coefficient [m^3/(mol•s)]
k_p	propagation rate coefficient [m^3/(mol•s)]
k_t	rate coefficient of termination [m^3/(mol•s)]
k_{tc}	rate coefficient of termination by combination [m^3/(mol•s)]
k_{td}	rate coefficient of termination by disproportion [m^3/(mol•s)]
k_{tM}	chain transfer to monomer rate coefficient [m^3/(mol•s)]
GF	gel effect factor
h	droplet-continuous phase heat transfer coefficient
$h_{c/r}$	heat transfer coefficient between the droplets in a coalescence/redispersion event
I	initiator
$I*$	active initiator radical
M	monomer
$M_{c/r}$	collision-induced process
m	mass of droplet [g]
ni	total amount of initiator in the system
$n(v,\chi,t)$	population density function of the droplet population
N	a Poisson process counting the collision events
N	total number of droplets
P_i	the closed polymer chain with chain length i
P_n^*	active, growing polymer chain
$Q_{reaction}$	the generated heat in exothermic polymerization reactions
$Q_{transfer}$	the removal heat to the continuous phase
R_i	the growing polymer chain with chain length i
$S_{c/r}$	frequency of binary collisions of droplets
t	time [s]
T	temperature [K]
T_f	continuous phase temperature
υ	droplet volume [m^3]
υ_M	volume of monomer in a droplet [m^3]
υ_P	volume of polymer in a droplet [m^3]
V	volume of suspension
X	monomer conversion (%)
X_f	critical monomer conversion (%)

Greek symbols

$\theta_{c/r}$	contact time between the droplets in a coalescence/redispersion event
μ_k	kth moment of the dead polymer chains [mol/ m^3]
ν_k	kth moment of the polymer radicals [mol/ m^3]
$\psi_{c/r}$	temperature jump induced by a coalescence/redispersion event
ω	parameter (random number between 0-1)
ρ	density of drop

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