

# Temperature Control of Batch Suspension Polyvinyl Chloride Reactors

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A simulation program was developed to analyze the influence of temperature profiles of the continuous phase on the polymer properties and monomer conversion in suspension polymerization reactors of vinyl chloride. Polymerization reactions are highly exothermic and the quality of polymer products is really sensitive to the temperature of polymerization so that processing of batch suspension polymerization reactors by proper temperature control is an important requirement. The developed simulation program is suit-able to compute the required cooling energy exactly to avoid the unnecessary energy consumption, and to determine the proper cooling profile of temperature inside the polymerization reactor that is needed to produce high quality end-use polymers.

## 1. Introduction

Polyvinyl chloride (PVC) is one of the most important products of the polymer industry. Although PVC is produced on a large scale in industry it usually is processed in batch reactors of volumes up to 160 - 200 m<sup>3</sup> (Nagy and Agachi, 1997). In suspension polymerization of vinyl chloride the water-insoluble monomer containing oil-soluble initiator is dispersed in the continuous aqueous phase by a combination of intensive stirring and the use of small amounts of suspending agents (stabilizers) (Yuan et al., 1991). Since the polymerization reactions take place in the monomer droplets so droplets behave as individual micro-reactors. The properties of the end use polymer product depend significantly on the polymerization temperature therefore depend mostly on the temperature inside the droplets (Palau et al., 2013). Consequently, it is needed to develop a detailed model for suspension polymerization which contains micro-, meso- and macro-scale processes inside a polymerization reactor, forming a complex three-scale model.

The continuous deterministic chemical reactions take place at micro-scale which are disturbed by collisions induced meso-scale interactions: coalescence and break up of droplets (Palau et al., 2012), and component and heat transport between the colliding droplets. So time continuous processes and discrete event processes occur parallel inside the polymerization reactors. In order to take the interdependence of micro- and meso-scale processes into consideration, suspension polymerization of vinyl chloride is modeled by using the population balance approach. The population balance technique is widely used in modeling heterogeneous dispersed processes such as crystallization (Ramkrishna, 2000) and heterogeneous polymerization (Kotoulas and Kiparissides, 2006).

In this work, a detailed model of batch polymerization reactors of vinyl chloride, the meso-scale population balance equation is completed with the macro-scale heat balance equations for the continuous phase, as well as for the heat transport between the continuous phase and the cooling medium. The model equations are solved by a coupled continuous time–Monte Carlo method taking into consideration the heat transfer between the polymerizing droplets and the continuous phase as well.

## 2. Model development

The model developed contains micro-, meso- and macro-scale processes inside the polymerization reactor, forming a complex three-scale system.

1. Micro-scale: Polymerization reactions, related with the kinetic mechanism and micromixing occur at the micro-scale.
2. Meso-scale: At meso-scale occur the collisions induced coalescence and break up of droplets.
3. Macro-scale: At this scale, the overall mass and energy balances, heat and mass transfer from the reactor as well as the reactor dynamics and control is described.

### 2.1 Micro-scale model

The kinetics considers initiation, propagation, chain transfer to monomer and termination by combination and disproportionation, as shown in Table 1. Where  $I$  is the initiator,  $I^*$  the active initiator radical,  $k_d$  the initiator decomposition rate coefficient,  $k_p$  the propagation rate coefficient,  $k_t$  the rate coefficient for termination,  $k_{tM}$  is the chain transfer rate coefficient,  $M$  the monomer,  $R_i$  the growing polymer chain with chain length  $i$ ,  $P_i$  the closed polymer chain with chain length  $i$ . The initiation process involves the chemical decomposition of unstable peroxides or azo compounds into free radicals ( $k_d$ ) which can react rapidly with monomer to begin the propagation of a polymer chain ( $k_i$ ) (Sidiropoulou and Kiparissides, 1990).

The applied model is based on the two-phase model developed by Sidiropoulou and Kiparissides (1990). The key feature of this model is that PVC is practically insoluble in its monomer, and polymerization proceeds simultaneously in the two phases almost from the start of the reactions.

### 2.2 Meso-scale model

In suspension polymerization of vinyl chloride the micro- and meso-scale processes, i.e. the behavior of droplets population in a batch, well mixed at macro-scale, reactor is governed by the population balance equation (Lakatos, 2011):

$$\frac{\partial n(\nu, c, T, t)}{\partial t} + \frac{\partial}{\partial c} \left[ \frac{dc}{dt} n(\nu, c, T, t) \right] + \frac{\partial}{\partial T} \left[ \frac{dT}{dt} n(\nu, c, T, t) \right] = \mathbf{M}_b[n(\nu, c, T, t)] + \mathbf{M}_a[n(\nu, c, T, t)] + \mathbf{M}_{c/r}[n(\nu, c, T, t)] \quad (1)$$

where the second and third terms on the left hand side provide, respectively, the rates of continuous changes of the population density function due to the mass and heat effects of chemical reactions while the terms on the right hand side of Eq(1) provide, in turn, the rates of jump-like changes of population density function because of coalescence, break up and collision induced heat exchange between the colliding droplets (Lakatos, 2011).

### 2.3 Macro-scale model

In suspension polymerization, mass transfer between the dispersed and continuous phases is negligible, therefore the detailed model of the reactor consists of Eq(1) completed with the macro-scale heat balance equations for the dispersed and continuous phases, and the cooling medium making possible to analyze the effects of temperature changes of the continuous phase on polymer properties.

The heat balance for a droplet is

$$\rho_d C_{p,d} v_d \frac{dT_d}{dt} = v_d (-\Delta H_r) \cdot \mathbf{R}_r(c_d, T_d) - a_d h_{dc} (T_d - T_c) \quad (2)$$

where  $T_d$ ,  $\rho_d$ ,  $v_d$  and  $C_{p,d}$  are, respectively, the temperature, density, volume and heat capacity of a droplet,  $T_c$  is the temperature of the continuous phase,  $a_d$  is the surface of a droplet,  $h_{dc}$  is the heat transfer coefficient between a droplet and the continuous phase,  $\mathbf{R}_r$  and  $-\Delta H_r$  are the vectors of the reaction rates and reaction heats, and  $c_d$  is the vector of concentrations of species in a droplet.

Table 1: Schematics of the kinetic model (Sidiropoulou and Kiparissides, 1990)

Reaction	Reaction scheme	Rate coefficients
Initiation	$I \xrightarrow{k_d} 2I^*$	$k_d = 6.32 \cdot 10^{16} \exp(-15460/T)$ (1/min)
	$I^* + M \xrightarrow{k_i} R_1$	
Propagation	$R_i + M \xrightarrow{k_p} R_{i+1}$	$k_p = 3 \cdot 10^9 \exp(-3320/T)$ (L/(mol·min))
Chain transfer to monomer	$R_i + M \xrightarrow{k_{tM}} R_1 + P_i$	$k_{tM} = 5.78 \exp(-2768/T) k_p$ (L/(mol·min))
Termination	$R_i + R_j \xrightarrow{k_{tc}} P_{i+j}$	$k_t = k_{tc} + k_{td} = 7.8 \cdot 10^{13} \exp(-2190/T)$ (L/(mol·min))
	$R_i + R_j \xrightarrow{k_{td}} P_i + P_j$	

The convective heat transfer coefficient ( $h_{dc}$ ) is calculated by empirical expressions. The heat balance for the continuous phase takes the form:

$$\rho_c C_{p,c} \varepsilon V \frac{dT_c}{dt} = V \int_{T_{\min}}^{T_{\max}} \int_0^{c_m} \int_0^{V_m} a_d h_{dc} (T - T_c) n(v, c, T, t) dv dc dT - A_{cj} h_{cj} V (T_c - T_j) \quad (3)$$

where  $T_c$ ,  $\rho_c$ ,  $\varepsilon$  and  $C_{p,c}$  are, respectively, the temperature, density, volumetric ratio and heat capacity of the continuous phase,  $V$  is the volume of the suspension,  $h_{cj}$  and  $A_{cj}$  denote the coefficient and the effective surface of heat transfer between the continuous phase and the cooling medium. In Eq(3),  $T_j$  denotes the temperature of the cooling medium in the jacket, assuming a step-wise cooling process at the initial moment of time.

The heat balance for the cooling medium is

$$V_j C_{p,j} \rho_j \frac{dT_j}{dt} = C_{p,j} F_j (T_{j,in} - T_j) - A_{cj} h_{cj} V (T_c - T_j) \quad (4)$$

where  $F_j$ ,  $C_{p,c}$  and  $T_{j,in}$  denote, respectively, the mass flow rate, the heat capacity and the inlet temperature of the cooling medium.

The mixed set of the integral-differential Eq(1) with the ordinary differential Eqs(2)-(3) of macro-scale heat balances was solved by developing a Monte Carlo (MC) procedure (Bárkányi et al., 2013a) combining the deterministic processes of chemical reactions inside the droplets and the heat transfer in the continuous phase with the effects of random collisions of droplets.

## 2.4 Solution 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 (Zhao and Zheng, 2013). Here we used an event-driven MC method. The developed solution method is suitable to calculate the deterministic polymerization reactions and the stochastic meso-scale interactions of monomer droplets, simultaneously. Figure 1 presents the algorithm of solution which was described in details in a previous work (Bárkányi et al., 2013b).

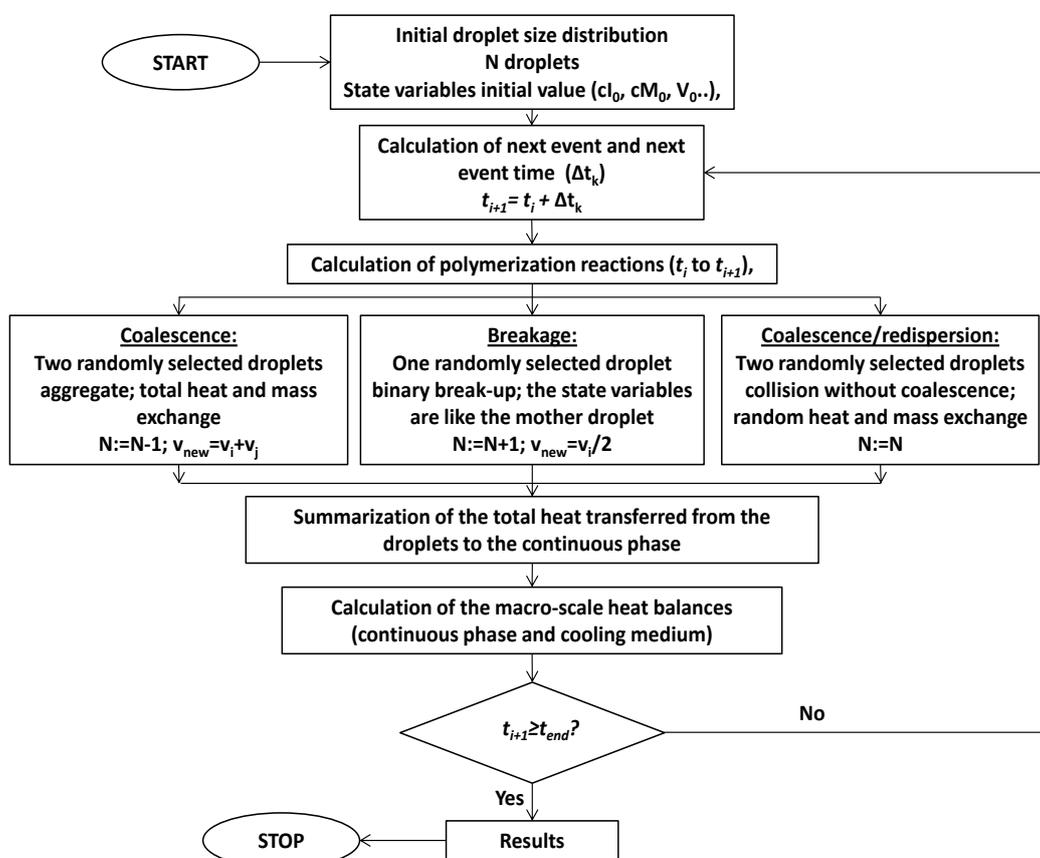


Figure 1: Algorithm of the solution

Notice that computations of concentrations and temperature changes due to the polymerization reactions in the droplets are carried out individually. The amounts of heat transferred from droplets to the continuous phase are computed simultaneously taking into account a correspondingly proportional mass of the continuous phase, and then all the segments of the continuous phase are mixed perfectly. After that the temperature of the continuous phase and cooling jacket are calculated by Eqs(3)-(4). It is assumed that the temperatures of both these phases are homogeneous as it is illustrated by Eqs(3)-(4).

### 3. Simulation results and discussion

The aim of this work was to analyze the influence of different temperature profiles of the continuous phase on the monomer conversion and polymer properties. As it is shown in Table 2, four different temperature profiles were analyzed by simulation. In cases p1 and p4 the temperature of continuous phase was kept constant at 323 K and 328 K, while in cases p2 and p3 the temperature of the continuous phase was changed along different temperature profiles during the polymerization.

In simulation experiments, the monomer droplets had initial droplet size distribution as were introduced in a previous work (Bárkányi et al., 2013b). Initially the initiator distribution was uniform, i.e. the initiator concentration was the same in all monomer droplets. All meso-scale droplet interactions were taken into consideration, i.e. collisions induced coalescence and coalescence/redispersion, and binary break up of droplets.

It is commonly assumed that in suspension polymerization heat transfer between the polymerizing droplets and the continuous phase is rapid, and both phases have the same average temperatures (Meyer and Keurentjes, 2005). Figure 2a shows the temperature profiles of the continuous and dispersed phases in the cases p1-p4 studied. From Figure 2a it is seen that the average dispersed phase temperature is higher than the continuous phase temperature in all cases. Figures 2b, 2c and 2d show the effects of different temperature profiles b) on the monomer conversion, c) on the weight and d) the number average molecular weights. It can be seen that there are significant differences in the monomer conversions and the polymer properties, too. Figures 2c and 2d illustrate well that the molecular weights are of lower value at higher temperature. We have to look for the reason of this phenomenon in the kinetics of polymerization. The number of polymer chains is lower at higher temperature because of the rate coefficients, as are shown in Table 1.

Since polymerization reactions take place in the dispersed phase and the properties of polymer are influenced by the temperature significantly it is important to control the temperature of polymerization. We can minimize the temperature rise in the dispersed phase if the temperature of the continuous phase is hold at constant value. So if we would like to keep the continuous phase temperature at a prescribed profile we have to guarantee the constant value of the continuous phase temperature during the process. The other goal of this work was to show how we can use the developed simulation program to calculate the favorable temperature profile of cooling jacket during a polymerization process.

The heat released from polymerization reactions can be calculated continuously in all reacting monomer droplets. After summarization we get the total heat  $Q_r$  produced by the reactions. If we would like to keep the continuous phase temperature at constant value than the distracted heat  $Q_j$  from the continuous phase has to be equal to  $Q_r$ . The needed cooling medium temperature can be calculated:

$$T_j = T_c - \frac{Q_r}{A_{cj}h_{cj}} \quad (5)$$

where  $T_c$  is known in every time step according to the temperature profile of the continuous phase.

The simulation experiments had the same initial conditions like the previous ones. Namely, the initial droplet size distribution was non-uniform, the initial initiator distribution was uniform and all meso-scale interactions were taken into consideration.

Table 2: Temperature profiles of the continuous phase during polymerization

Profile name	Temperature of continuous phase
p1	Constant 323 K
p2	Section 1: Constant 323 K from 0 min to 50 min Section 2: Linear change from 323 K to 328 K during 100 min Section 3: Constant 328 K from 150 min to 200 min
p3	Linear change from 323 K to 328K during 200 min
p4	Constant 328 K

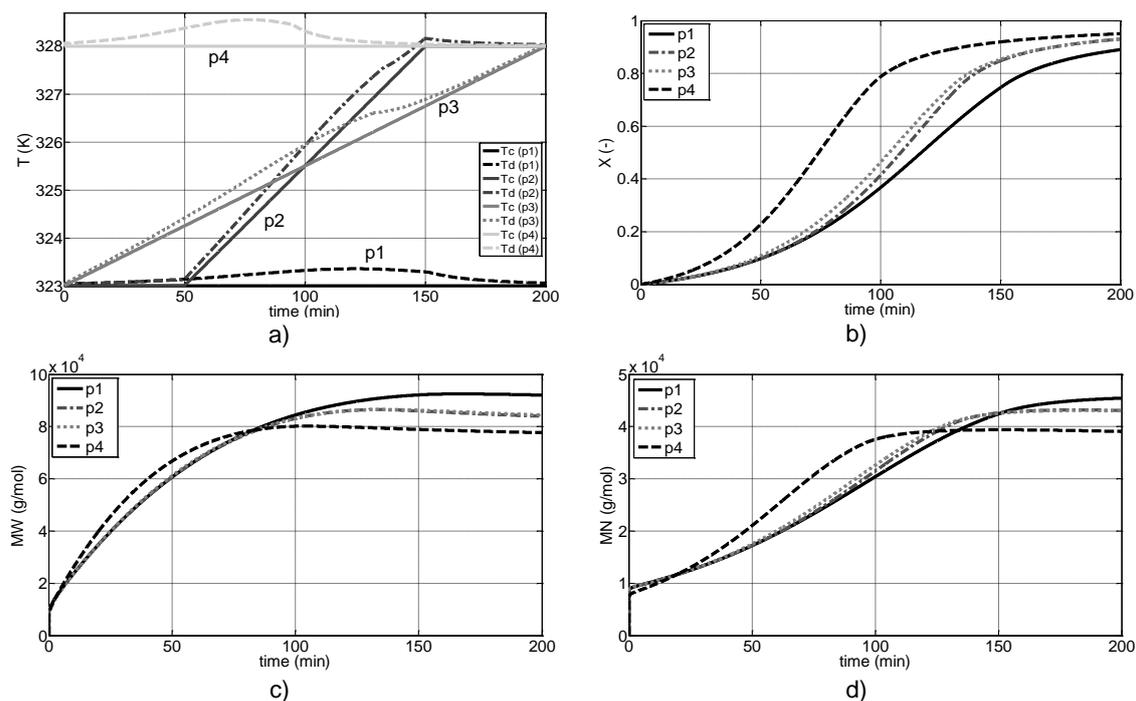


Figure 2: Temperature profiles (a) of the continuous (continuous lines) and the dispersed phase (dashed lines) in the reactor. The conversion profiles (b); the weight- (c) and number (d) average molecular weight profiles by different continuous phase temperature profiles. The amount of initiator was 0.0029 mole % based on monomer, initially the initiator distribution was uniform

Figure 3 presents an example of calculation of the favorable temperature profile of cooling medium. In this case, the goal was to keep the continuous phase temperature at constant value 323 K during the process. Figure 3a shows the required temperature profile of the cooling medium. It can be seen that in that case the average temperature rise in droplets, as it shown in Figure 3b, was smaller than 0.5 K. This temperature change does not cause significant changes in the polymer properties. So we do not need to use cooler medium in the jacket. Using this procedure we can minimize the utilization of the cooling energy during the temperature control of suspension polymerization reactors.

#### 4. Conclusions

A population balance equation was presented for modeling the time continuous and discrete event processes of droplets population in suspension polymerization of vinyl chloride, completed with the macro-scale heat balance equations for the continuous phase and the cooling medium. The developed coupled

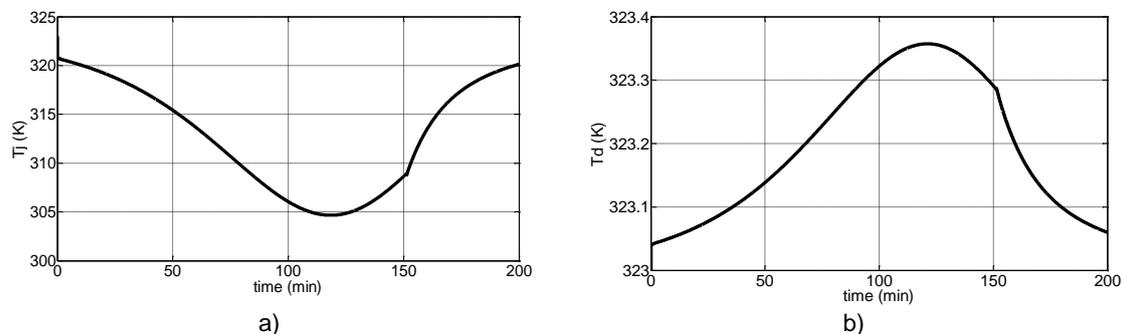


Figure 3: The temperature profile in cooling jacket (a) and the average temperature rise in droplets (b) during polymerization. The continuous phase temperature was kept constant 323 K. The amount of initiator was 0.0029 mole % based on monomer, initially the initiator distribution was uniform

continuous time-Monte Carlo method allowed computing the heat transfer processes between the polymerizing droplets and the continuous phase.

The simulation results show that the developed model and simulation program is suitable to analyze the influence of different temperature profiles of the continuous phase on the monomer conversion and polymer properties. Through an example was illustrated that the simulation program is suitable to calculate the favorable temperature profile of the cooling medium for the prescribed continuous phase temperature profile.

Using this procedure we can minimize utilization of the cooling energy for temperature control of suspension polymerization reactors.

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