



# Continuous Function Approximation for Dispersed Phase Distribution in Suspension Polymerization

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Polymers are nowadays used in a multitude of applications, many of the latter being in close relationship with the polymer molecular mass distribution (PMMD), which could be affected by the way the polymer was obtained: bulk, solution, emulsion or suspension. The polymers produced in heterogeneous processes strongly depend not only on the polymerization kinetics, but also on the heterogeneous phase distribution, closely related to the operating conditions. This means that the drop size distribution, which is affected by the stirring rate, surfactant concentration and monomer-polymer solution characteristics, is relevant in the final polymer properties. The PMMD determines the polymer processing techniques, which require that the input material has certain specified features. The present work shows the interdependency between PMMD and drop distribution through the heat transfer process between drops and the continuous phase.

## 1. Introduction

The suspension polymerization of styrene has been widely studied in the past. Not only that its kinetics is relatively simpler as compared to ethylene or buthyl acrylate polymerization, for example, for which chain transfer to polymer is quite common, but the product from this suspension process is the precursor for expanded polystyrene, largely used in isolation applications.

In spite of the simplicity of the reaction kinetics for this monomer, the fact that it is polymerized by a suspension procedure adds complexity to the process. The monomer drops suspended in the continuous medium interact with one another and with the internals of the reactor, thus being broken or coalescing. The consequence is a permanent change of the drop sizes inside the reactor; the drop density distribution remains the same, i.e. uniform, normal or Pareto, but its mean and dispersion change (Koutoulas and Kiparissides, 2006).

The population balance technique is widely used in modelling heterogeneous dispersed processes such as grinding, crystallization (Bastos Borba Costa et al., 2007), and heterogeneous polymerization (Chen et al., 1999; Jahanzad et al., 2005; Vale and McKenna, 2005). The characteristic length of the dispersed phase (drop volume in the present case) is the property most commonly used in describing the population distribution; for a closed-system suspension polymerization, coalescence and breakage are the two mechanisms leading to a change in the property distribution. When coupled with the polymerization kinetics, this change may affect the heat transfer. This in turn, together with coalescence, influences PMMD and eventually the characteristics of the final product.

The usefulness of predicting the drop size distribution in a heterogeneous process consists in properly controlling the process to obtain the desired product properties. Consequently, polymer beads with imposed plasticizing and heat transfer capabilities may be obtained (Meyer and Keurentjes, 2005).

The present work deals with the influence of the particle size distribution on the peculiarities of styrene polymerization inside the drops.

## 2. Model equations

The model development is based on the styrene polymerization system, as previously presented by Lavric and Jinescu (1988). The reaction is assumed to take place in a discontinuous mechanically stirred reactor, with jacket cooling. The flowrate of the thermal agent is controlled by a PID regulator, so that the temperature profile is maintained as close to a reference temperature as possible.

It should be noted that the reaction topochemistry for a suspension process implies polymerization inside the drops. Therefore, in order to quantify the influence of the particle size on the polymerization development, partial differential equations were written for temperature, monomer and initiator, with respect to position inside the drop.

In model development, the following assumptions were made:

- a) Initiation takes place by peroxide initiator decomposition and, above 90 °C, by self-initiation of the monomer, with third-order kinetics with respect to the monomer. The total initiation rate is computed as the sum of the two individual rates.
- b) The termination reaction only takes place by recombination.
- c) The chain transfer reaction only takes place with the monomer molecules.
- d) Active centres obey the quasi-steady-state assumption.
- e) All the reactions take place in the suspended drops.
- f) Drops are isotropic.
- g) Diffusion is the only mechanism acting along the drop radius.
- h) The geometry of the reactor is cylindrical, that of the jacket is annular.
- i) The physical properties of the suspension change with conversion and particle distribution.
- j) The reaction volume varies with the polymer-monomer fraction.
- k) Suspension drops and particles are of spherical shape.

### 2.1 Kinetic model

The kinetics considers initiation, both by peroxide decomposition and by monomer self-initiation, propagation, termination by combination and chain transfer with the monomer, as shown in Table 1.

### 2.2 Material balance

The monomer (1) and initiator (2) mass balance equations were rendered dimensionless, where:  $\mu$  is the ratio between the instantaneous monomer concentration  $M$  and the initial concentration  $M_0$ ;  $\nu$  is the ratio between the instantaneous initiator concentration  $I$  and the initial concentration  $I_0$ . The time length characteristic for the drop (3) depends upon its radius  $R_d$ .  $R_p$  and  $R_{it}$  are the propagation and initiator decomposition rates, respectively.

### 2.3 Thermal balance

The heat generated in the drops as a consequence of the polymerization reaction should be removed by the heat transfer process between the former and the continuous phase. Any imbalance leads to a change in the drop temperature. The dimensionless form of the thermal balance is given by equation (4), where  $\theta$  is the dimensionless temperature, the ratio of the instantaneous and the reference temperatures, while  $q_v$  denotes the heat generation in the volume (5).

In order for the thermal balance to be used in the model, the physical properties (density, heat capacity, thermal conductivity and viscosity) of the reaction mixture were computed as a function of composition and temperature (Lavric and Jinescu, 1988). Then, the dimensionless Reynolds, Prandtl, and Nusselt numbers were computed for the suspension inside the reactor, in order for the partial heat transfer coefficient to be obtained. The partial heat transfer coefficient for the cooling water flowing through the jacket was computed analogously.

Table 1: Schematics of the kinetic model

| Reaction                    | Reaction scheme                            | Rate constant                                    |
|-----------------------------|--|--|
| Peroxide initiation         | $I \xrightarrow{k_{iI}} 2R_1$              | $k_{iI} = 1.0554 \cdot 10^{14} \exp(-14949.5/T)$ |
| Self-initiation             | $M \xrightarrow{k_{iM}} 2R_1$              | $k_{iM} = 2.19 \cdot 10^5 \exp(-13810/T)$        |
| Propagation                 | $R_n + M \xrightarrow{k_p} R_{n+1}$        | $k_p = 1.051 \cdot 10^7 \exp(-3557/T)$           |
| Termination                 | $R_x + R_z \xrightarrow{k_t} R_{z+x}$      | $k_t = 1.255 \cdot 10^9 \exp(-844/T)$            |
| Chain transfer with monomer | $R_x + M \xrightarrow{k_{tr.M}} R_1 + P_x$ | $k_{trm} = 2.31 \cdot 10^6 \exp(-6337/T)$        |

$$\frac{\partial \mu}{\partial \tau} = 4 \pi \frac{D_M}{D_T} \frac{1}{\sigma^2} \frac{\partial}{\partial \sigma} \left( \sigma^2 \frac{\partial \mu}{\partial \sigma} \right) - \frac{R_p \tau_T}{M_0} \quad (1)$$

$$\frac{\partial v}{\partial \tau} = 4 \pi \frac{D_I}{D_T} \frac{1}{\sigma^2} \frac{\partial}{\partial \sigma} \left( \sigma^2 \frac{\partial v}{\partial \sigma} \right) - \frac{R_{iI} \tau_T}{I_0} \quad (2)$$

$$\tau_T = \frac{4 \pi R_d^2}{D_T} = \frac{4 \pi R_d^2 \rho_S C p_S}{\lambda_S} \quad (3)$$

$$\frac{\partial \theta}{\partial \tau} = \frac{4 \pi}{\sigma^2} \frac{\partial}{\partial \sigma} \left( \sigma^2 \frac{\partial \theta}{\partial \sigma} \right) + q_v q^* \quad (4)$$

$$q_v = (-\Delta H_{rp}) R_p; \quad q^* = \frac{\tau_T}{T_{ref} \rho_S C p_S} \quad (5)$$

However, for the reactor to remain nearly isothermal, a proportional-integral-differential (PID) regulator was implemented. Its purpose is to control the thermal agent flowrate by taking into account the difference between the instantaneous and the reference temperatures, the history of the system, and the evolution tendency of the polymerization reactor's temperature. Due to technological (pump capacity) and safety reasons, the thermal agent flowrate has an upper and a lower, non-zero, boundary, respectively.

#### 2.4 Model solution

The model containing three partial differential equations (variation along the radius for temperature and monomer and initiator conversions) and two ordinary differential equations (variations of reactor temperature and of the difference between reactor temperature and reference temperature) has been solved in Matlab, using the "pdepe" function for the PDE system and the "ode15s" function for the ODE system.

In order to underline the influence of drop size distribution on heat transfer and conversion in the polymerization process, the drop distribution was assumed to be uniform or Pareto-like; the size interval [0.5, 2] mm was divided into classes of equal length. The partial differential equations had to be solved for all the diameters corresponding to a class distribution. Simulations were performed for various dimensions for comparison.

### 3. Results and discussion

Simulations showed that temperature gradients within the particle are practically non-existent, since drop radius is very small. However, it was revealed (Figure 1) that drop size does influence the temperature of both the drops and the continuous medium (water). Figures 1 a. and b. refer to mono-dispersed drops with the highest and the lowest diameters, respectively. For large diameters the

reactor temperature is higher than for small ones. As the drop radius increases, its specific area decreases so it is less efficiently cooled by the continuous medium of the suspension. Still, the drop remains quasi-isothermal. Consequently, the higher drop temperature will eventually rise the overall temperature in the reactor. The small drops are cooled more efficiently, meaning that they do not accumulate that much heat, due to their larger heat transfer area.

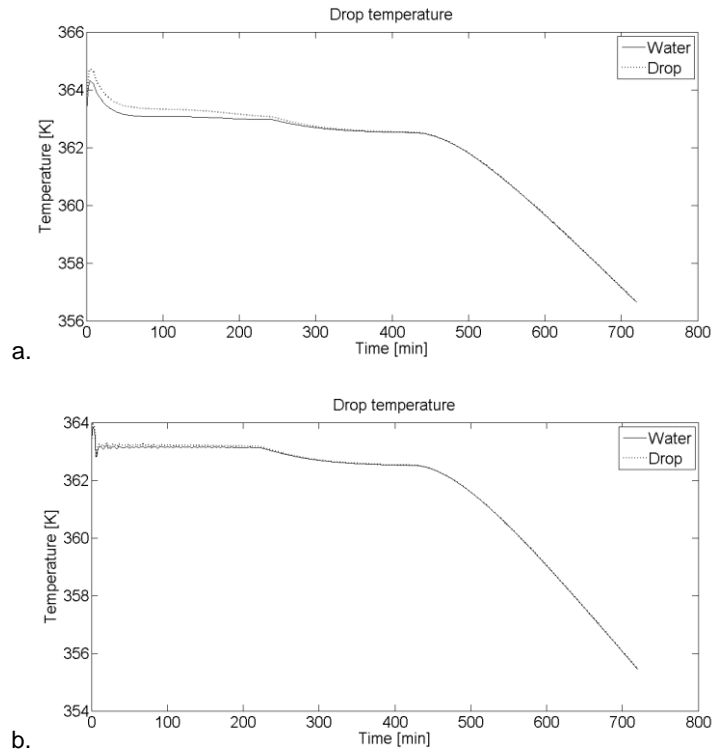


Figure 1: Influence of the size and number of the drops on the temperature evolution inside the reactor: a. 2 mm drop case; b. 0.5 mm drop case

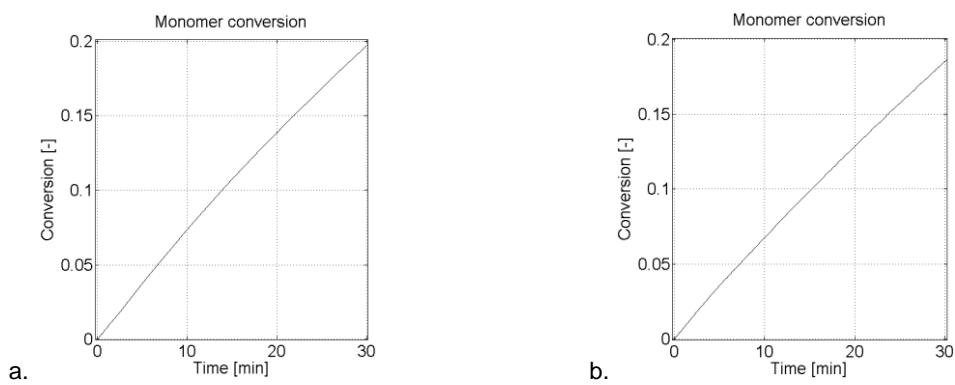


Figure 2: Influence of the drop size on the conversion evolution inside the reactor: a. 2 mm drop case; b. 0.5 mm drop case

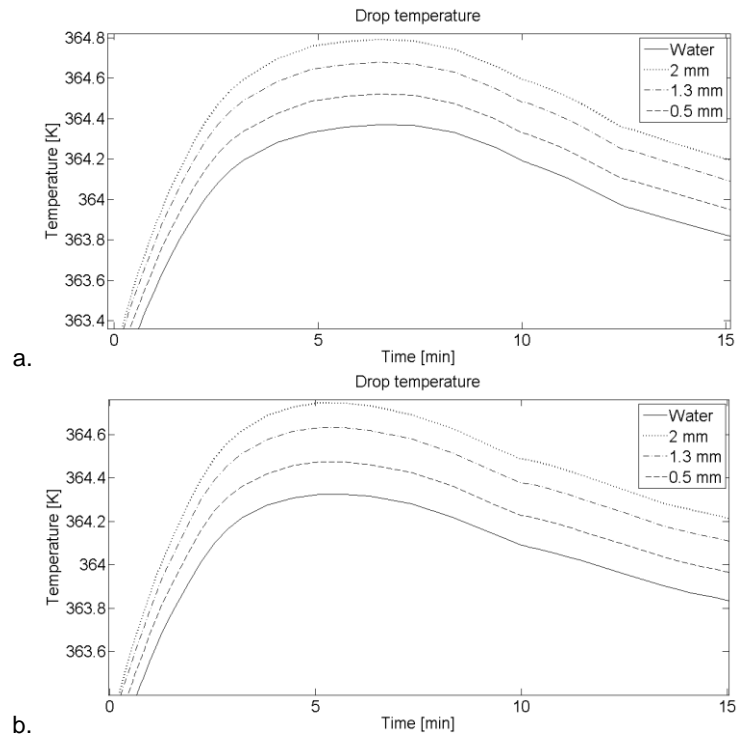


Figure 3: Temperature evolution for the 3-class case, for a. uniform and b. Pareto distributions

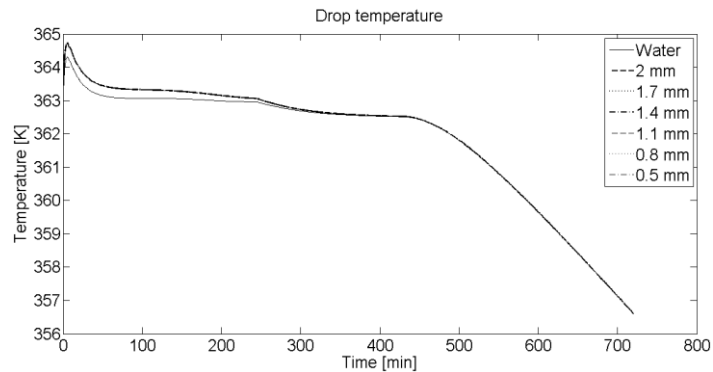


Figure 4: Temperature evolution for the 6-class case, for both distribution types

The slight differences concerning the temperature evolution within the drop at the beginning of the process lead to different conversion evolution for the two cases mentioned above. Figures 2 a. and b. show higher conversion for large drops within the first 30 minutes of reaction. Their higher reaction temperature (Figure 1) is responsible for this increased reaction rate and faster conversion.

The type of the distribution is another factor with impact on the temperature evolution. A three-class case is shown in Figure 3. A uniform distribution implies the existence of equal number of drops for each drop size, while a Pareto distribution assumes an exponential decay of drops' number with their size. The comparison of Figures 3 a. and b. leads to the conclusion that, although the temperature differences between the drops of the specified classes stay unchanged for the two types of distributions, the fraction of drops of given sizes does matter. The Pareto distribution yields a slightly lower temperature for water and for drops. Comparison of Figures 3 and 1 b. leads to the remark that

the coexistence of drops of different sizes has an impact on the temperature of the individual drops and on that of the continuous medium.

At the reactor level, the thermal agent flowrate is permanently adapted to the reactor's temperature through the PID controller. Due to the limiting capacity of the pumping system, this flowrate, and thus the transferred heat, cannot exceed a maximum value. Therefore, when the cooling system has attained this limitation, and when the generated heat is high, the temperature in the reactor increases.

When only small drops are present in the dispersion – see Figure 1 b. – the temperature has a slight increase during the first 15 minutes of the reaction. The heat generated is smoothly transferred to the continuous medium and then taken by the thermal agent. The temperature gradient between the two phases increases when large drops are present within the dispersion. Since the heat flow to the thermal agent is approximately the same in both cases, the temperature of the continuous medium increases due to this gradient. Eventually, the heat generated within the drops decreases faster when the drops are large, causing more rapid cooling of the entire system than for the small drops case.

When six drop sizes are considered, however, there are no differences, not only between successive classes, but also between the largest and the smallest drop size (Figure 4). The result is the same for both types of distributions. This means that, as long as drops cover the entire size range, temperature is constant with respect to drop radius. Uniformity is achieved, as far as temperature – and conversion – is concerned, regardless of the drop radius, for continuous distributions.

#### **4. Conclusions**

This work showed the importance that the particle size distribution has over the development of the suspension polymerization process. It has been proven that the presence of a higher number of large particles in the suspension leads to deviations of the reaction temperature with respect to the reference value. The implications are also extended on the level of monomer conversion, since reaction rates exponentially depend on temperature. The use of the two continuous functions describing uniform and Pareto distributions yields the same result for large numbers of drop sizes, and differing performance in the cases of fewer drop sizes distributed within the same range.

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