MODELLING OF POLYMER PARTICLE FORMATION
USING POPULATION BALANCE MODEL

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The paper presents a study of formation of the primary particle size distribution in suspension "powder" polymerization of vinyl chloride. The process is modelled by means of a population balance model, and the primary particle size distribution inside the polymerizing monomer droplets is determined by analysing the population balance equation, governing the nucleation, growth, and aggregation of the primary particles, using the moment method.

The infinite set of moment equations obtained by moment transformation was closed using a sum aggregation kernel, and for numerical experimentation a second order moment equation model was used. The results show how important are to choose the correct parameters in production of poly(vinyl chloride) by suspension polymerization. Changing the parameters a bit the quality of product may change significantly.

The results presented in the paper illustrate well that the population balance model can be used for describing the process and a number its properties with sufficient accuracy.

Keywords: Suspension polymerization, vinyl chloride, population balance equation, moment equation, simulation.

Introduction

Plastics are major industrial goods used in the building, construction, packaging, transportation, electronic , etc., idustries. Plastics can be in general classified into thermoplastics, thermosetting resins and engineering plastics.

Commodity thermoplastics are manufactured in large volumes and comprise polymers such as polyvinil chloride, polyethylene (low and high density), isostatic polypropylene, polystyrene.

The main basic material of the plastics manufacturing is the polyvinyl chloride. Due to its unique morphological characteristics, PVC can be combined with a number of additives resulting in materials exhibiting a broad range of end-use properties.

The morphological properties of the PVC grains are determined by the following process variables: polymerization temperature, quality of agitation, type and concentration of the surface active agents, so it is needed to studying the effects of these variables.

The quality of PVC is primarily characterized by the morphology of the polymer grains. The morphology of PVC grains, produced by the suspension polymerization process, is determined by the grain shape, and grain size distribution, the average grain porosity and pore size distribution as well the accessibility of the grain's internal pores. It should be noted that PVC morphology greatly affects its handling, processing and application characteristics. Grain porosity largely influences the removal of unreacted VCM and plasticizer uptake by the PVC grains during processing.

The morphology of the PVC grains is depended on the properties of primary particles. The primary particle size distribution influences the porosity of the final grains to a large degree. So, the first goal is modelling the primary particle size distribution in suspension polymerization.

The population balance approach has proved to be an adequate tool for model-based investigation of suspension polymerization by tracking the time evolution of polymer particles [1, 2, 3]. This approach was applied also by Bárkányi [4] and Bárkányi et al. [5] to study formation of the primary particle size distribution in suspension polymerization of vinyl chloride.

The aim of the paper is to present the population balance equation and its second order moment equation reduction used in analysing formation of the primary particle size distribution in suspension polymerization of vinyl chloride. The infinite set of moment equations obtained by moment transformation is closed using an approximate sum aggregation kernel. Results obtained by numerical experimentation by a second order moment equation model illustrate well that the population balance approach can be used for describing the process.

The mechanism of the suspension PVC process

The suspension polymerization of vinyl chloride monomer (VCM) proceeds in two phases: the first one is the monomer-rich phase and the other one is the polymer-rich phase. So, the model includes the polymerization processes in the two phases and the describing of the component transfer between the phases. [6, 7, 8].

Previously published papers [9, 10, 11, 12, 13, 14, 15] on the morphology of PVC grains have postulated the following five-stage kinetic-physical mechanism, shown in *Fig. 1,* to describe the nucleation, stabilization, growth, ad aggregation of PVC primary particles.
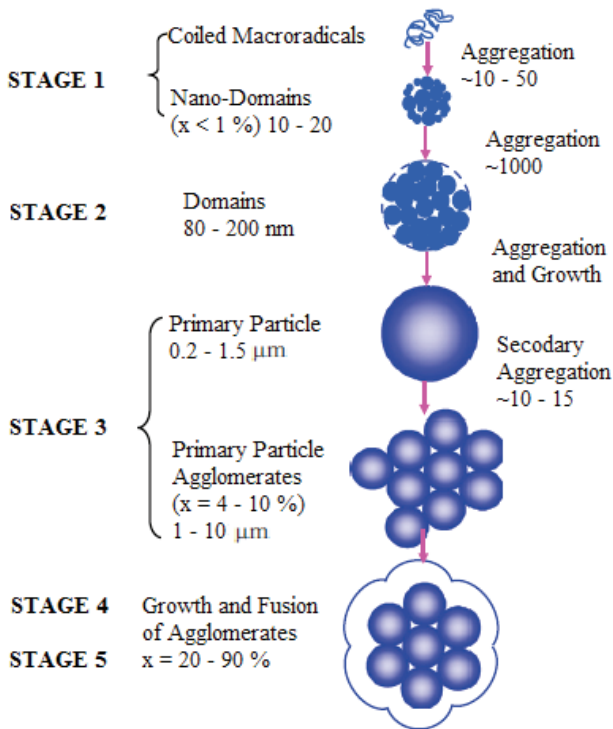

Figure 1: Evolution of primary PVC particles

During the first polymerization stage (VCM conversion range: $0 < X < 0.01\%$), primary radicals, formed via thermal decomposition of initiator molecules, rapidly react with monomer to produce polymer chains that almost instantaneously become insoluble in the monomer phase. The polymer chains precipitate out of the continuous VCM phase when they reach a specific chain length. It has been postulated that approximately 10–50 polymer chains are subsequently combined together to form nano-domains also called basic particles. The nano-domains are swollen with monomer and have an initial diameter of about 10–20 nm.

In stage two (VCM conversion range: $0.01 < X < 1\%$), the formation of PVC domains, also called primary particle nuclei, takes place. Because of the limited stability of the domains, they rapidly undergo coagulation leading to the nucleation of the primary particle nuclei. The initial size of these primary particle nuclei has been found to be in the range of 80–100 nm. Typically, a primary particle nucleus may contain about 1000 nano-domains. The primary particle nuclei carry sufficient

negative electrostatic charges to form stable colloidal dispersions in the monomer phase.

In stage three (VCM conversion range: $1 < X < 20\%$), growth and aggregation of the primary particles occur. The size and the number of the primary particles depend on the growth rate and the electrostatic-steric stability of the primary particles. The latter attribute decreases as the monomer conversion increases. Massive aggregation of the primary particles results in the formation of a continuous three-dimensional primary particle network within the VCM droplet. The three-dimensional primary particle network structure, i.e. its initial porosity and mechanical strength depend on the size and the number of primary particles, the electrostatic and steric forces between the primary particles, the polymerization temperature and the polymer viscoelastic properties.

In stage four (VCM conversion range: $20<X<70$-75%), the growth and fusion of the primary particles continues. That is, the primary particles increase in size due to polymerization and also undergo substantial fusion. Both processes result in a continuous decrease in particle porosity. The primary particles continue to grow until the disappearance of the separate monomer phase.

Finally, in stage five (VCM conversion range: 70-$75<X<90$-95%), polymerization continues only in the monomer swollen polymer phase, however, at a lower rate, until the monomer has been depleted. At the final VC conversion, the size of the individual primary particles is in the range of 1–1.5 μm while the size of the primary particle aggregates is about 3–10 μm.

The model

Despite the importance of the primary particle size distribution (PPSD) on the development of PVC grain morphology, there is only a limited number of quantitative models dealing with the dynamic evolution of the primary particles in terms of process variables. [7]

In general, the dynamic evolution of the particles size distribution in a particulate process can be obtained from the solution of a population balance equation (PBE). The population of the primary particles can be expressed in terms of a number density function, $n(v, t)$ that represents the number of particles per unit volume of monomer droplet phase in the differential size interval $(v, v+dv)$. For a dynamic system under-going particle nucleation, aggregation, and growth, the evolution of the particle size distribution is described by the following non-linear integral-differential PBE:

$$\frac{\partial n(v,t)}{\partial t} + \frac{\partial (G(v,t)n(v,t))}{\partial v} = \delta(v-v_0)S_0(t)$$

$$+ \int_0^{v/2} \beta(v-u,u)n(v-u,t)n(u,t)du \qquad (1)$$

$$- \int_0^{\infty} \beta(v,u)n(v,t)n(u,t)du$$

where $G(v, t)$ is the particle growth rate due to polymerization in the polymer-rich phase, $S_0(t)$ is the

nucleation rate of primary particles of volume v_0 in the monomer-rich phase, and $\beta(v, u)$ is the aggregation rate kernel for particles of volume u and v. Eq. (1) satisfies the following initial and boundary conditions:

$$n(v, 0) = 0, \text{ at } t = 0, \text{ and } n(0, t) = 0, \text{ at } v = 0.$$

In order to solve Eq. (1), the functional forms of $G(v, t)$ and $S_0(t)$ need to be first determined.

According to Kiparissides [3] the primary particle nucleation and growth rates is given by

$$G(v,t) = \frac{M_w R_{pp}}{\rho_m X} v \tag{2}$$

$$S_0(t) = \frac{R_{pm} M_w}{\rho_p (1 - \varphi_m) v_0} \tag{3}$$

where X is the monomer conversion, φ_m is the volume fraction of monomer in the polymer-rich phase, M_w is the molecular weight of VCM, ρ_m and ρ_p are the corresponding monomer and polymer densities, R_{pm} and R_{pp} denote the respective polymerization rates in the monomer and polymer-rich phase. Note that the growth rate is linear with respect to the particle volume, typical of bulk polymerization systems and depends on R_{pp} and, thus, on time.

The polymerization rates in the monomer and polymer-rich phase, R_{pm} and R_{pp} can be calculated from a kinetic model [10, 16, 17]. In the present study, a simplified kinetic model was applied [18]:

$$R_{pm} = k_d [M][I]^{1/2} \frac{(1 - BX_f)}{X_f} \frac{(X_f - X)}{X_f(1 - X)} \tag{4}$$

$$R_{pp} = k_p [M][I]^{1/2} P \frac{(1 - X_f)X}{X_f(1 - X)} \tag{5}$$

where k_d is the rate constant for initiator decomposition, $[M]$ is the monomer concentration, $[I]$ is the initiator concentration, and X_f is the VCM conversion at which the separate monomer-phase disappears.

Calculation of conversion X depends on if X is smaller or larger than the critical conversion X_f. Calculation of X is provided by the following equations: If $X < X_f$:

$$\frac{dX}{dt} = \frac{1 + QX}{(1 - BX)^{1/2}} K[I_0]^{1/2} \times \exp(-k_d t / 2) \tag{6}$$

If $X > X_f$:

$$\frac{dX}{dt} = \frac{PK}{1 - X_f} [I_0]^{1/2} \frac{(1 - X)^2}{(1 - BX)^{1/2}} \times \exp(-k_d t / 2) \tag{7}$$

where $K = k_p (f k_d / k_t)^{1/2}$ and f is the initial factor, and $Q = AP - A + 1$.

The dimensionless coefficients of the kinetic model:

$$A = (1 - X_f) / X_f \tag{8}$$

$$B = (\rho_p - \rho_m) / \rho_m \tag{9}$$

$$P = \frac{\left(\sqrt{2 f k_d / k_t}\right)_p}{\left(\sqrt{2 f k_d / k_t}\right)_m} \approx 27 - 0{,}14(T - 273) \tag{10}$$

For determination of the primary particle size distribution can we used the gamma distribution function:

$$y = f(x | a, b) = \frac{1}{b^a \Gamma(a)} \cdot x^{a-1} \cdot e^{-\frac{x}{b}} \tag{11}$$

where a and b parameters which can be determined from the moment equations, and Γ is the gamma function.

Solution and results

The numerical solution of Eq. (1) is very difficult while analytic solution is not known. Thus we solved it by using moment transformation.

It was assumed that $b(v, u) = b_0(v + u)$, where $b_0 = \frac{\dot{\gamma}}{\pi}$ and $\dot{\gamma} = \frac{\pi}{8 R_d} \frac{\Delta v}{(1 + \mu_1 / \mu_2)}$,

where R_d is the radius of the monomer droplets, Δv is the relative velocity of the droplets, μ_1 and μ_2 are the viscosity of water- and polymer phases.

The moment equations are:

Equation for the zero order moment:

$$\frac{\partial \mu_0(t)}{\partial t} = -b_0 \cdot \mu_1(t) + S_0(X(t)) \tag{12}$$

where: μ_0 is the zero order moment of volume V:

$$\mu_0 = \int_0^\infty n(V, t) \, dV \tag{13}$$

Eq. (12) provides the time evolution of the total number of particles.

Equation for the first order moment:

$$\frac{\partial \mu_1(t)}{\partial t} - G_0(X(t)) \cdot \mu_1(t) = V_0 \cdot S_0(X(t)) \tag{14}$$

where: μ_1 the first order moment of volume, V:

$$\mu_1 = \int_0^\infty V \cdot n(V, t) \, dV \tag{15}$$

Eq. (14) gives the total volume of particles.

Equation for the second order moment:

$$\frac{\partial \mu_2(t)}{\partial t} - 2 G_0(X(t)) \cdot \mu_2(t) = 2 b_0 \frac{\mu_1(t) \cdot \mu_2(t)}{\mu_0(t)} + V_0^2 \cdot S_0(X(t)) \tag{16}$$

μ_2 has not got any physical meaning but the knowledge of these properties is needed for characterizing the system. The initial conditions of moment equations are:

$$\mu_0(0) = \mu_1(0) = \mu_2(0) = 0; \quad t = 0.$$

The set of moment equations were solved in MatLab environment, and the parameter values used were obtained from the literature. As the model provided adequate results we examined how the results regarding the

moments varied changing the parameters. In this case, examination of process was focused on the analysis of the b_0's effect. This parameter influences the rate of aggregation in the process. We varied parameters R_d and Δv since, because the kinetic parameters were constant it did not influence the conversion and the time variation of the concentration of initiator. But changing these parameters influenced the moments significantly.
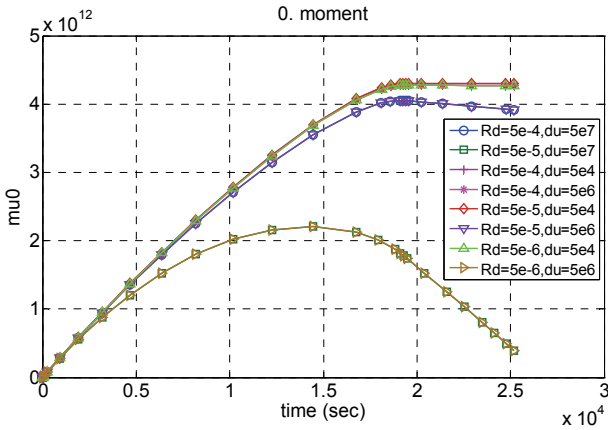

Figure 2: Evolution in time of the zero order moment

Fig. 2 shows the time evolution of the zero order moment in function of changing of parameters. The differences between the running down of curves are on account of the changing of the rate of aggregation. The bigger the rate of aggregation the fewer particles there are in the system, because they cohere.
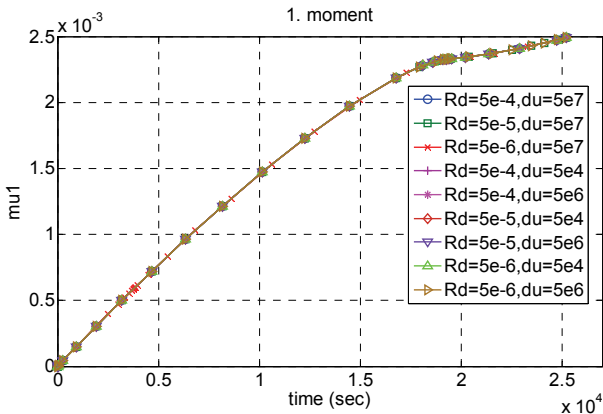
Figure 3: Evolution in time of the first order moment

In *Fig. 3* one can see that changing the parameters in question do not influence the first order moment. Because the first order moment denotes the total volume of particles it is not a surprising fact since the total volume of particles is independent on aggregation.

In *Fig. 4* we see two different types of curves. If the rate of aggregation is able to neglectful compared to the rate of nucleation, the curve monotonously increases, otherwise it goes through a maximum, and after it starts decreasing.

After that we studied the dependence of behaviour of the process as a function of the parameter b_0. In *Figs 5* and *6* it can be seen that changing the parameter b_0

influence only the zero and second order moments so we studied these two moments.
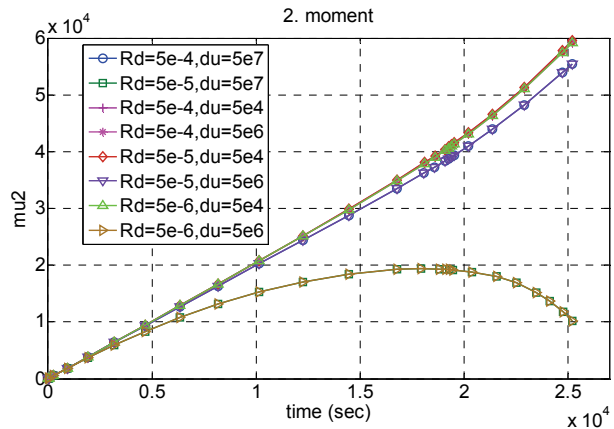

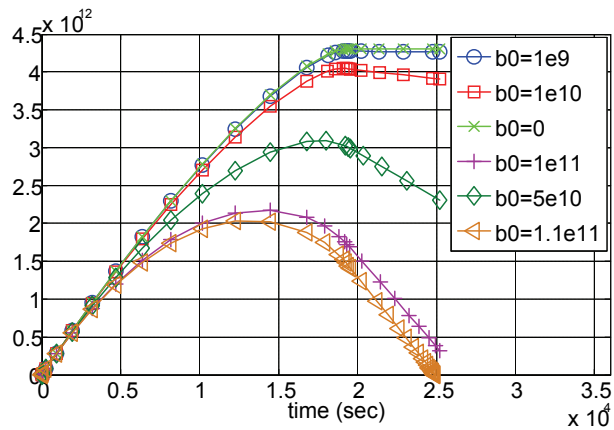*Figure 4:* Evolution in time of the second order moment

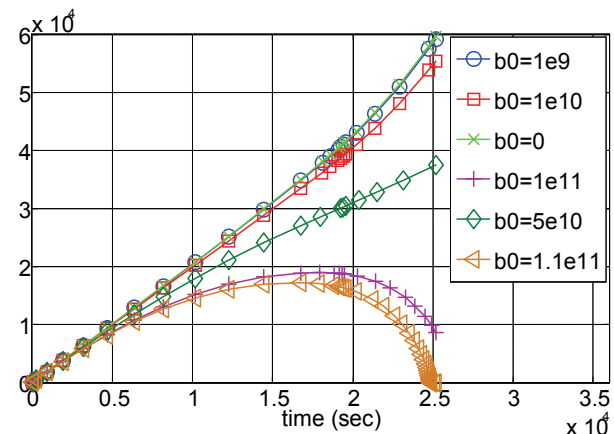*Figure 5:* Evolution in time of the zero order moment

Figure 6: Evolution in time of the second order moment

Figs 5 and 6 show that evolution of the process depends strongly on the ratio of growth and aggregation rates. With increasing aggregation rate the number of particles in the system decreases significantly. As the aggregation rate passes a critical value the process likely exhibits gelation phenomenon what would be the subject of a future interesting study.
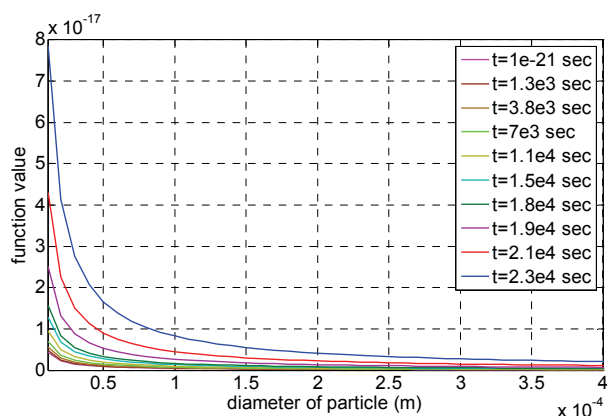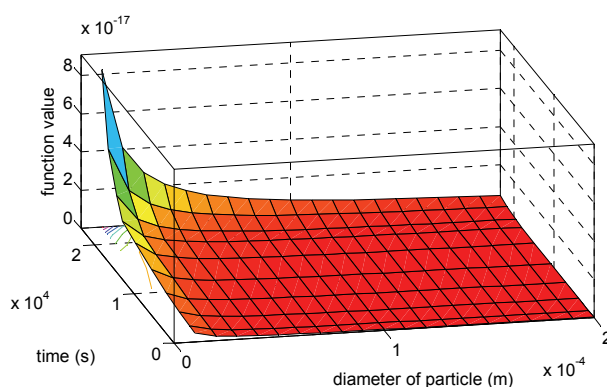
Figure 7: Primary particle size distribution

Figure 8: Primary particle size distribution (3D)

Figs 7 and *8* show the primary particle size distribution. It can be seen when the polymerization is going, the diameter of particles continually grows.

Conclusions

A population balance model and a second order moment equation system was presented for analysing formation of the primary particle size distribution in suspension "powder" polymerization of vinyl chloride. The model involves nucleation, growth and aggregation of primary particles having significant influence on the properties of polymer grains.

The infinite set of moment equations obtained by moment transformation was closed using an approximate sum aggregation kernel, and for numerical experimentation a second order moment equation model was used. The results revealed that it is very important to choose the correct parameters in production of poly(vinyl chloride) by suspension polymerization since changing the parameters a bit the quality of product may change significantly.

The results presented in the paper illustrate well that the population balance model can be used for describing the process and a number its properties with sufficient accuracy.

SYMBOLS

A, B constants
a, b parameters of gamma-distribution
D diameter of particle, m
f iniciator factor
G growth rate in volume-scale, m^3/s
I_0 initial value of iniciator concentration, $kmol/m^3$
K constant
k_d the rate constant for initiator decomposition constant, 1/s
k_p monomer phase propagation constant, 1/s
k_t termination rate constant, 1/s
m weight, kg
M monomer concentration, $kmol/m^3$
n number density function, db/m^6
P, Q constants
r radius of particle, m
R_d radius of VCM droplet, m
R_{pm} polymerization rate in the monomer phase, $mol/s/m^3$
R_{pp} polymerization rate in the polymer phase, $mol/s/m^3$
S_0 nucleation rate, $db/m^3/s$
t time, s
T temperature, K
u volume, m^3
v volume, m^3
v_0 volume of PVC basic particles, m^3
X conversion
X_f critical conversion

GREEK LETTERS

β aggregation rate kernel, m^3/s
δ Dirac-delta function
μ_0 0. moment
μ_1 1. moment
μ_2 2. moment
ρ density, kg/m^3
φ_m monomer volume fraction in the polymer phase
Γ gamma function

SUBSCRIPTS

m monomer
p polymer

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