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Modelling and simulation of suspension polymerization of vinyl chloride via population balance model

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ABSTRACT

A detailed population balance model is presented for suspension polymerization of vinyl chloride in an isothermal batch reactor perfectly mixed on macrolevel. Coalescence and breakage of monomer droplets, as well as mass exchange of species between the droplets induced by collisions, termed micromixing, are also included into the model forming a complex three-scale system. The resulted population balance equation is solved by coupling the deterministic continuous time computation of polymerization reactions inside the droplets with the random coalescence and breakage events of droplets using Monte Carlo simulation. The results obtained by simulation revealed that aggregation, breakage and micro-mixing of species induced by droplet collisions affect the process significantly.

1. Introduction

Suspension polymerization is used for commercial manufacture of many important polymers including polyvinyl chloride (PVC), polymethyl methacrylate and polystyrene. In this method, droplets of a monomer-containing phase are dispersed randomly in a continuous liquid phase by intensive stirring and the polymer is produced inside the droplets. PVC is produced by powder polymerization since PVC is insoluble in the VC monomer hence it immediately precipitates out formatting a separate phase. However, in suspension polymerization monomer droplets may break up as well as coalescence with each other continuously in the turbulent flow field of the reactor. As this breakage-aggregation process of droplets proceeds parallel with polymerization inside the droplets their interactions may have significant effects on the final particle size distribution of polymer powder what is one of the most important issues in suspension polymerization (Hashim & Brooks, 2004; Kotoulas & Kiparissides, 2006).

The population balance approach can be applied to describe the temporal evolution of droplet size distribution adequately (Kotoulas & Kiparissides, 2006). The continuous population balance equation (PBE) is an equation governing the evolution of the population density function as a result of different particle mechanisms like nucleation, growth, aggregation and breakage. The PBE has diverse application, like crystallization, precipitations, aerosol dynamics, microbial fermenters and polymer reactors. In modelling suspension polymerization, however, applying this approach requires solving the PBE, describing the droplet size distribution simultaneously with computing the polymerization reactions occurring inside the droplets. In addition, during the course of coalescence of droplets some equalization of species, i.e. micromixing may take place what complicates the problem even more.

As analytical solutions of PBEs are available in very few cases, due to the importance of PBE, many numerical solution methodologies have been proposed to solve the one dimensional PBE. A partial list consists of discretization methods, finite elements, moment methods and generalized method of moments. In many cases of industrial interest, in order to fully characterize the powder some other particle properties like surface area, chemical composition and crystallinity are needed in addition to particle size (volume). These multidimensional problems are very difficult to solve using direct numerical solutions. There are several numerical methods available that satisfy the accuracy requirement (Bove, Solberg, & Hjertager, 2005). Among them are the methods of classes (Kumar & Ramkrishna, 1996a, 1996b; Vanni, 2000), the quadrature method of moments (Marchisio, Vigil, & Fox, 2003; McGraw & Wright, 2003), the direct quadrature method of moments (Marchisio & Fox, 2005) and the standard method of moments using the cumulant-neglect closure (Lakatos, Bárkányi, & Németh, 2011; Lakatos, 2011).

The Monte Carlo (MC) methods are often selected as solution methodology for complex multidimensional population balance models where direct numerical solution becomes very difficult (Irizarry, 2008). The MC simulation of a PBM consists of a simple

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Notation

A	parameter
b_b	resulting volume of breakage
b_c	resulting volume of coalescence
$\boldsymbol{c}$	vector of concentration variables in a droplet
c_I	concentration of initiator (mol/m^3)
c_M	concentration of monomer (mol/m^3)
F_ω	distribution function
F_Θ	distribution function
I	initiator
I^*	active initiator radical
k_d	initiator decomposition rate coefficient (1/s)
k_I	initiation 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))
M	monomer
$\boldsymbol{M_c}$	coalescence
$\boldsymbol{M_b}$	breakage
$\boldsymbol{M_{ex}}$	collision induced exchange of mass of species
M_w	molecular weight of monomer (g/mol)
$n(v,\boldsymbol{c},t)$	population density function of the droplet population
n_{M0}	initial value of monomer (mol)
n_M	value of monomer (mol)
N	total number of droplets
P_υ	factor
P_i	the closed polymer chain with chain length i
R_i	the growing polymer chain with chain length i
S_c	frequency of coalescence of droplets
S_b	frequency of break up of droplets of given volumes
S_{ex}	frequency of binary collisions of droplets of volumes υ and υ' resulting in exchange of mass without aggregation
t	time (s)
υ	droplet volume (m^3)
X	monomer conversion (%)
X_c	critical monomer conversion (%)

Greek symbols

ε_m	volume fraction of monomer in a droplet
θ	properties of the viscous turbulent carrier phase characterized by this parameter
μ_j	$j$thmoment of deadpolymerchains
ν_j	$j$thmoment of livepolymerchains
ρ_m	density of monomer
ρ_p	density of polymer
ω	parameter (random number between 0 and 1)

Subscript

1	monomer rich phase
2	polymer rich phase

stochastic game that models the evolution of the population. These methods are robust and easy to implement, and their advantage is that they capture inherent fluctuation for systems away from the thermodynamic limit. Therefore, since suspension polymerization is a complex process in the mathematical model of which a multidimensional population balance equation plays significant role it appears to be advisable combining the modelling attempt of suspension polymerization of VC with an MC solution method.

The aim of the paper is to present a population balance model for suspension polymerization of VC and to analyze the model and the process by applying a MC method taking into account breakage and aggregation of droplets as well as micromixing induced by droplet binary collisions. Break up into two equal volumes of droplets, binary aggregation and random mass exchanges between the colliding droplets are assumed, while the kinetic data of VC polymerization are taken from the literature (De Roo, Wieme, Heynderickx, & Marin, 2005).

2. Model development

2.1. General

Suspension polymerization is usually carried out in batch tank reactors. At the start of the process, two immiscible liquids are mixed to produce a dispersion of monomer droplets in a continuous aqueous phase. Two cases can be distinguished as regards the addition of initiator. In the first case, the monomer and initiator are homogenized first, the mixture is filled in the reactor, and subsequently the reactor is heated to the reaction temperature. An advantage of this process is that the distribution of initiator in the monomer is perfect while its disadvantage is that the polymerization reactions occur under non-isotherm conditions during the heating stage. Therefore, the properties of the end-use polymer might be not uniform. In the other case, first the monomer is filled in the reactor, the suspension is heated to the polymerization temperature and thereafter the initiator is added to the suspension. The advantage of this method is that the polymerization reactions occur under isothermal conditions and the properties of the end-use polymer usually are uniform. The disadvantage of this process is that the initiator distribution in the monomer droplets may be not perfect. In this work we analyze the second case and investigate the effects of non-perfect initiator distribution by simulation.

By adding initiator which is dissolved in the monomer droplets where the polymerization reactions are going on, the radical polymerization of VCM is started. 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. The most commonly used suspending agents for vinyl chloride suspension polymerization are water-soluble polymers such as hydroxypropyl mthylcellulose (HPMC) and partially hydrolysed polyvinyl acetate, commonly called PVA (Saeki & Emura, 2002). The adsorption of such molecules at the monomer-water interface reduces the interfacial tension and hence reduces the energy required to form droplets (Zerfa & Brooks, 1996).

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 reactor, subsequently two relevant processes occur in parallel in the reactor. Polymerization reactions inside the droplets (Bárkányi, Németh, & Lakatos, 2011), having rates depending on the actual concentrations and temperature in droplets, form a continuous in time deterministic process. Simultaneously with that, random binary collisions may occur between the droplets moving in the reactor space the frequency of which depends on their number in a unit volume of the reactor, and, despite the stabilizers, collision induced interactions may result in aggregation or only in interchange of some mass of species. Besides,