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A multiscale CFD-PBM coupled model for the kinetics and liquid–liquid dispersion behavior in a suspension polymerization stirred tank

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ABSTRACT

Suspension polymerization of methyl methacrylate (MMA) has been considered as a liquid–liquid reactive polydispersity system, which involves the complex multiphase flow behavior at multiple time and length scales. The polymerization kinetic characteristics (i.e., gel effect and glass effect) and liquid–liquid dispersion phenomena (i.e., breakage and coalescence of liquid droplets) appearing in this process make the study of suspension polymerization complicate. In this work, a three dimensional (3D) multiscale model including Eulerian–Eulerian two-fluid model, polymerization kinetics model, population balance model (PBM) and some other constitutive models was developed to elaborate those multiscale phenomena in polymerization course. The current model was validated using the reported data in terms of conversion, molecular weight as well as droplet Sauter diameter. The developed model was then employed to investigate the influence of key operating conditions on polymerization kinetic characteristics and liquid–liquid dispersion phenomena. Furthermore, the effects of reactor structure on droplet breakage and coalescence were studied in detail. This simulation work may contribute to the preparation of polymer products and the scaling up of stirred tank polymerization reactors with multiphase flow and multiscale characteristics.

1. Introduction

Suspension polymerization can be implemented using a heterogeneous radical polymerization technology. It is commonly carried out in batch agitated vessels and adopted in industrial processes to produce many commercial resins, including polyvinyl chloride (PVC), polystyrene (PS) as well as polymethyl methacrylate (PMMA) (Brooks, 2010; Ni et al., 2001; Vivaldo-lima et al., 1997; Vonka et al., 2016). This process uses mechanical agitation and suspending agent to mix a monomer or the mixture of monomers in the aqueous phase. As polymerization proceeds, monomer droplets experience a viscous syrupy state, and finally form polymer spheres (Kalfas et al., 1993).

For a suspension polymerization process, reactive liquid–liquid dispersion is a characteristic behavior (Jahanzad et al., 2004, 2005b). Both polymerization reactions and liquid–liquid suspension dispersions are involved in this process (see Fig. 1). Since the oil-soluble initiators are usually used in this process, the polymerization reactions thus take place only in the monomer droplet phase, and their kinetics behaves like that of bulk polymerization for water insoluble or slightly water soluble monomers (Kalfas and Ray, 1993). Liquid–liquid dispersion in a stirred tank reactor is another important behavior to be well controlled in suspension polymerization. The droplet size determined by a dynamic equilibrium between breakage and coalescence rates is an important feature for the application of the polymer products. Therefore, a holistic description of suspension polymerization requires fundamental insights in both polymerization kinetics and liquid–liquid dispersion phenomena, which are vital to the productivity and stability of the process. Nevertheless, the intrinsic complexities of such process has led to difficulties in in-depth interpretation of the process characteristics in terms of polymerization and particle kinetics.

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Nomenclature

a_b, a_c	Model parameters in PBM
b_c	Model parameters in PBM
$b(\lambda)$	Breakage rate (1/s)
$B(L; x, t)$	The birth rate of droplets diameter L (m/s)
$c(\lambda, L)$	Coalescence rate (1/s)
C_D	Drag coefficient
C_p	Heat capacity (J/(mol K))
$C_\mu, C_{1\varepsilon}, C_{2\varepsilon}$	Coefficients in turbulence model
d	Droplets diameter (m)
d_{32}	The Sauter diameter (m)
$D(L; x, t)$	The death rate of droplets diameter L (m/s)
f	Initiator efficiency
F	The interphase force (N/m^3)
g	Gravitational acceleration (m/s^2)
$G_{k,m}$	Production of turbulent kinetic energy
$G(L)$	The growth rate of droplets diameter L (m/s)
h	Specific enthalpy (kJ/(kg K))
I	Identity matrix
k	Turbulence kinetic energy (m^2/s^2)
κ_{ad}	Thermal conductivity (W/(m K))
k_b, k_c	Model parameters in PBM
k_d	Decomposition rate constant (1/s)
k_{in}	Initiation rate constant for monomer adding to primary radical (L/(mol s))
k_p	Chain propagation rate constant (L/(mol s))
k_{t0}	Combinative termination rate constant for primary radical adding to primary radical (L/(mol s))
k_{tc}	Combinative termination rate constant (L/(mol s))
k_{td}	Disproportional termination rate constant (L/(mol s))
k_{tr}	Chain transfer rate constant (L/(mol s))
k_{tR}	Combinative termination rate constant for primary radical adding to radical chain with length r (L/(mol s))
L	Droplet diameter (m)
$n(L; x, t)$	Length number density function (m)
Nu	Nusselt number
P	Pressure (Pa)
Pr	Prandtl number
q	Heat flux (W/m^2)
Q_{ad}	Intensity of heat exchange between two phases (W/(m^3 s))
r	Chain length
r_n	Number average chain length
r_w	Weight average chain length
R	Universal gas constant (J/(mol K))
Re	Reynolds number
t	Flow time (s)
T	Temperature (K)
v	Velocity (m/s)
Ve	Elasticity parameter
We	Weber number
Y_0	Elasticity parameter

Greek letters

ρ	Density (kg/m^3)
μ	Dynamic viscosity (Pa s)
β	Daughter droplet distribution
ω_b, ω_c	Breakage and coalescence frequency respectively (1/s)
ω_m	The mth-order moment of propagating radical
λ_b, λ_c	Breakage and coalescence efficiencies respectively
λ_m	The mth-order moment of dead chains
θ	Elasticity parameter
Θ	Elasticity parameter
α	Volume fraction
ϕ_d	Volume fraction of dispersed phase
κ	Thermal conductivity (W/(m K))
τ	Shear stress (N/m^2)
ΔQ	Heat produced from polymerization reaction (J/mol)
σ	Interfacial tension (N/m)
Ω	Efficiency parameter
ε	Turbulence energy dissipation rate (m^2 s^3)

Many review articles have described all aspects of suspension polymerization kinetics in detail (Brooks, 1990; Vivaldo-lima et al., 1997; Yuan et al., 1991). The numerical simulations and experiments of MMA aqueous suspension polymerization were systematically performed by Ray's group (Kalfas and Ray, 1993; Kalfas et al., 1993, Zhang and Ray, 1997). They developed a two-phase reaction kinetics model to characterize the influence of partially water-soluble monomers on suspension polymerization kinetics. Simulation results agreed well with experimental data in terms of the total monomer conversion. They found that polymerization and two-phase droplet dispersion were decoupled under the circumstance of low dispersed phase holdup. Moreover, monomer solubility and inter-phase mass transfer played a significant role in a suspension polymerization process. Many simulations about vinyl chloride suspension polymerization kinetics were carried out by Kiparissides et al. (1997) and Krallis et al. (2004). The dynamic behaviors of a suspension polymerization batch reactor were described in detail based on the proposed model. In a similar manner, Wieme et al. (2007a,b) and Roo et al. (2005) simulated the vinyl chloride suspension polymerization reactors ranging from laboratory scale to pilot and even industrial scales. Model predictions matched well with the experimental data. Recently, Xie and Luo (2016, 2017) have simulated MMA suspension polymerization based on a CFD-PBM multiscale model. A full-scale coupled model was put forward to characterize multiscale flow fields in the batch stirred reactor and the particle properties. Particle dynamics were simultaneously simulated. In conclusion, previous models already gave predictions that quantitatively agree well with experimental data.

Additionally, many attentions have been paid to liquid–liquid dispersion in suspension polymerization that determines the particle size distribution and the end use of polymer products. Many review articles relating to the discussions of liquid–liquid dispersion phenomena have been published (Chesters, 1991; Liao and Lucas, 2009, 2010). A great quantity of experimental and simulation works have been conducted by Kiparissides' group (Alexopoulos et al., 2002; Alexopoulos and Kiparissides, 2007; Chatzi et al., 1991; Kotoulas and Kiparissides, 2006; Maggioris et al., 1998, 2000; Saliakas et al., 2008) to explore the droplet size distribution (DSD) in suspension polymerization. Since the droplet size was determined by growth, breakage and coalescence rates which were significantly affected by the local flow conditions, a two-compartment PBM was developed to establish the relationship between turbulence non-homogeneity and DSD. The simulation results were shown to be in accordance with the experimental data. Furthermore, different numerical methods were employed to solve the dynamic evolution of the droplet/particle size distribution. Jahanzad (2004), Jahanzad et al. (2004, 2005a,b, 2008) elaborated the evolution of particle diameter and size distribution in the course of suspension polymerization based on the proposed model. Four characteristic inter-