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Modelling of Vinylidene Fluoride Emulsion Polymerization

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Abstract

In the present study, a comprehensive mathematical model for the emulsion polymerization of vinylidene fluoride (VDF) in a semi-batch reactor is developed. The predictive capabilities of the model are demonstrated by a direct comparison of model predictions with experimental data on the monomer feed rate, monomer conversion, molecular weight averages and molecular weight distribution, mean particle size and particle size distribution, for a batch VDF emulsion polymerization reactor. It is shown that there is a good agreement between model predictions and experimental data.

Keywords: Polymerization, emulsion, vinylidene fluoride, model, PSD

1. Introduction

Poly(vinylidene fluoride) (PVDF) is an important fluoropolymer which exhibits a unique combination of properties including excellent chemical resistance, high thermal stability, and good mechanical as well as piezoelectric properties. Due to its superior properties, PVDF is widely used as wire and cable insulation material, as sheet and melt-cast films for electronics, in fittings, valves and pumps, etc. PVDF is produced commercially by emulsion and suspension polymerization processes.

In this paper, a comprehensive mathematical model of the VDF emulsion polymerization process is developed. The model can predict the molecular (e.g., molecular weight distribution, copolymer composition, etc.) and morphological (e.g., particle size distribution) properties of the latex in terms of process operating conditions. The mathematical model includes: a) full description of the kinetics and the material balances, b) calculation of the gel effect based on the generalized free-volume theory (Keramopoulos and Kiparissides, 2002), c) thermodynamic determination of monomer partitioning and pressure calculation, d) physical description of the crystalline phase and the amount of crystallinity, and e) calculation of the particle size distribution.

Detailed experimental measurements on the polymerization rate, the monomer feed rate, the molecular weight distribution and the particle size distribution were provided by ATOFINA. The experiments were carried out in a 30 lt semi-batch reactor. The polymerization pressure was kept constant throughout the reaction by introducing additional monomer into the reactor. Initiator and chain transfer agent were added at the beginning and at various instances.

2. Modelling of VDF Emulsion Polymerization

The mathematical modelling of emulsion polymerization reactors has been the subject of a great number of publications (Gilbert, 1995). Nevertheless, the development of a comprehensive mathematical model, capable of predicting the molecular (e.g., molecular weight distribution, copolymer composition, etc.) and morphological (e.g., particle size distribution) properties of the latex is not a trivial task, for there is a number of physical and chemical phenomena, which cannot be experimentally assessed and, thus, modeled. The present mathematical model of the VDF emulsion polymerization includes: a) all the differential/algebraic equations describing the kinetics of polymerization as well as the evolution of the particle size distribution, b) the calculation of the gel effect based on the generalized free-volume theory, c) the thermodynamic part (monomer partitioning and pressure calculation) and d) the physics of the crystalline phase (amount of crystallinity, etc.).

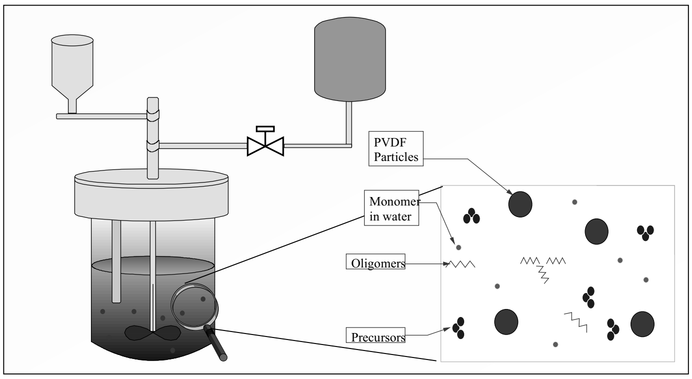

Figure 1. Emulsion Polymerization of VDF

2.1 Kinetic Mechanism of Emulsion Polymerization

The kinetics mechanism of VDF emulsion polymerization can be described by the following elementary reactions:

Reactions in the aqueous phase

Decomposition of initiator: $I \xrightarrow{k_i} 2I\cdot$

Propagation in the aqueous phase: $P_i^w\cdot + M_j^w \xrightarrow{k_{pij}} P_j^w\cdot$

Termination in the aqueous phase: $P_i^w\cdot + P_j^w\cdot \xrightarrow{k_{tij}} Q^w$

Chain transfer to monomer in the phase: $P_i^w\cdot + M_j^w \xrightarrow{k_{tmij}} P_j^w\cdot + Q^w$

Chain transfer to CTA in the aqueous phase: $P_i^w\cdot + X^w \xrightarrow{k_{xix}} X^w\cdot + Q^w$

Reactions in the polymer phase

Propagation in the polymer phase: $P_i^p \cdot + M_j^p \xrightarrow{k_{pij}} P_j^p \cdot$

Chain transfer to monomer in the polymer phase: $P_i^p \cdot + M_j^p \xrightarrow{k_{tmij}} P_j^p \cdot + Q^p$

Chain transfer to agent in the polymer phase: $P_i^p \cdot + X^p \xrightarrow{k_{xix}} X^p \cdot + Q^p$

Termination in the polymer phase: $P_i^p \cdot + P_j^p \cdot \xrightarrow{k_{tij}} Q^p$

In the above elementary reactions the symbols P_i^w, P_i^P, Q^w, Q^p denote the “live” and “dead” polymer chains that are present in the aqueous (w) and polymer (p) phase, respectively. The subscript “i” denotes the type of “live” polymer chain in multi-component systems (i.e., active polymer chains ending in monomer of type “i”). Following the original developments of Richards et al. (1989), the consumption rate of the various reaction species can be written.

Table 1. Polymerization rate expressions

Rate of Initiator consumption	$R_{Iw} = k_I C_{iw}$
Rate of monomer consumption	$R_{pie} = R_{ppie} + R_{pwie}$
Rate of monomer consumption in the particulate phase	$R_{pie} = \sum_{j=1}^{m} (k_{p_{ji}} + k_{f_{ji}}) C_{j^\bullet p} C_{ip} V_p / V_e$
Rate of monomer consumption in the aqueous phase	$R_{pie} = \sum_{j=1}^{m} (k_{p_{ji}} + k_{f_{ji}}) C_{j^\bullet p} C_{ip} V_p / V_e$
Rate of chain transfer agent consumption	$R_{pxe} = \sum_{j=1}^{m} k_{f_{jx}} C_{j^\bullet p} C_{xp} V_p / V_e$
Rate of generation of in situ generated surfactant	$R_{ge} = (1 - f)(R_{Iw} + R_d) V_w / V_e$
Total rate of radical entry in the emulsion phase	$R_{Ie} = R_{ew} V_w / V_e$
Rate of “dead” copolymer production	$R_{qe} = R_{pxe} + \sum_{i=1}^{m} \sum_{j=1}^{m} k_{f_{ij}} C_{i^\bullet p} C_{jp} V_p / V_e$

It should be noted that although the polymer particle phase is the main locus of polymerization, monomer consumption in the aqueous phase is also included. Thus, the total monomer consumption rate in the emulsion phase, R_{pie}, is given by the sum of the monomer consumption rates in the polymer, R_{ppie}, and the aqueous phase, R_{pwie}.

3. The Population Balance Equation

In order to describe the development of the PSD in an emulsion polymerization reactor a population balance approach is employed (C. Kiparissides *et al*, 2004). The distribution of particles is considered to be continuous over volume and is described by a particle number density function, $n_V(V,t)$, which represents the number of particles within a differential volume size range, V to V+dV, per unit volume of latex. The rate of change of the number density function is described by the following nonlinear integro-differential population balance equation:

$$\frac{\vartheta n_V(V,t)}{\vartheta t}+\frac{\vartheta[G_V n_V(V,t)]}{\vartheta V}=\frac{1}{2}\int_{V_0}^{V-V_0}\beta(V-U,U)n_V(V-U)n_V(U,t)dU$$

$$-\int_{V_0}^{V_\infty}\beta(V,U)n_V(V)n_V(U,t)dU-n_V\frac{1}{V}\frac{dV}{dt}+\delta(\frac{V}{V_m}-1)r_m(t) \qquad (1)$$

where $\beta(U,V)$ is the coagulation rate kernel between particles of volumes U and V, $G_V(V,t)$ is the growth rate of a particle of volume V at time t and $r_m(t)$ is the particle nucleation rate. The second term on the LHS represents the particle growth due to reaction in the latex particle (polymer phase) and the two integral terms on the RHS represent changes in particle size due to aggregation. The third term on the RHS describes the effect of dilution due to the semi-batch feeding of the monomer.

The boundary condition for the general condition is given by: $n_V(V,0)=0$. For an unseeded emulsion polymerization, the initial condition is given by: $n_V(V_0,t)=0$. It should be noted that the present emulsion polymerisation model determines the average number of radicals per particle for each particle-size of the PSD. The general dynamic PBE is solved simultaneously with the kinetics equations using the orthogonal collocation on finite elements method (Alexopoulos et al., 2004).

4. Simulation Results

The predicting capabilities of the present model were demonstrated by a direct comparison of model predictions with experimental data on the monomer feed rate, monomer conversion, mean particle size and particle size distribution, as well as the molecular weight distribution for a VDF emulsion polymerization reactor. All polymerizations were performed at $T=83^0C$ in a 30lt semi-batch reactor.

In the first experiment, the initiator (potassium persulfate) and the chain transfer agent were added in the initial pre-emulsion. As the reaction proceeds, the reactor pressure was kept constant by continuous addition of VDF monomer. In Figs. 2a and 2b, the total amount of VDF monomer fed into the reactor as well as the feed rate are compared to model predictions. As can be seen, the experimental data and the model predictions are in excellent agreement. In Fig. 3a, the calculated pressure drop profile is compared to the experimental data on the reactor pressure. The predicted number and weight-averaged molecular weight distributions are depicted in Fig 3b.

Experimental data from a number of different experimental recipes were compared to the model predictions. In particular, the effect of multiple initiator and CTA shots during the course of the reaction was studied in detail. In Fig. 4, the experimental VDF feed rates are compared to model predictions for two different recipes.

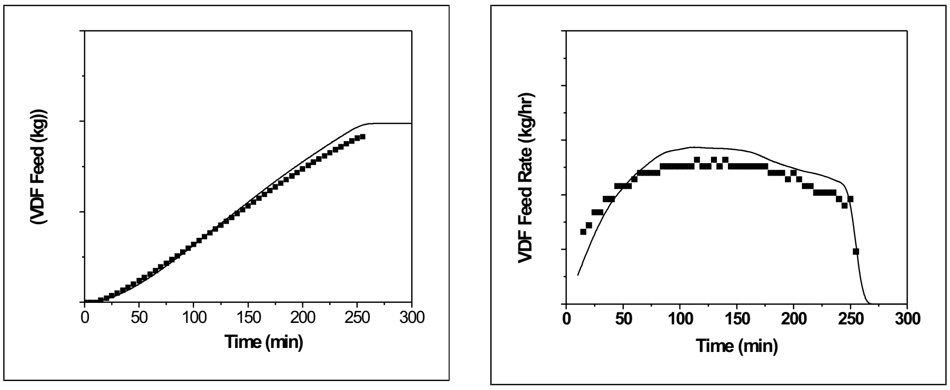

Figure 2. VDF emulsion polymerization (a) Total VDF feed and (b) VDF Feed Rate

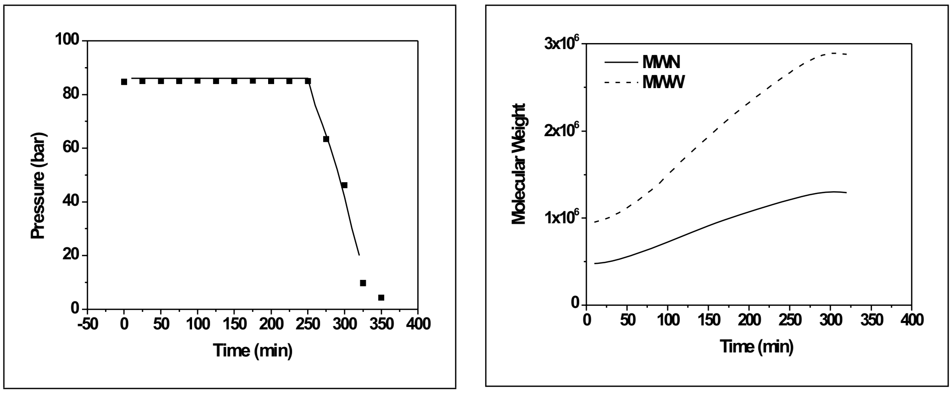

Figure 3. VDF emulsion polymerization (a) Reactor pressure (b) Average molecular weight

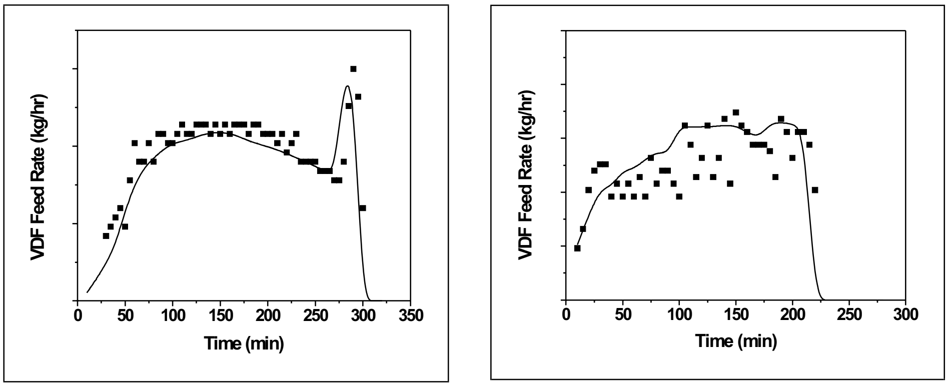

Figure 4. VDF emulsion polymerization (a) Two initiator shots (b) Multiple initiator and CTA shots

In Fig. 4a, an additional amount of initiator is fed into the reactor at 45 and 275min. As can be seen, the experimental data agree very well with the numerical predictions. It is clear that in the late stages of polymerization, the addition of initiator results in a substantial increase in the reaction rate. Frequently, a CTA is added during the course of the reaction to modify the MWD. However, the addition of CTA can decrease the rate of reaction due to an increase in the production of CTA-terminated radicals which are less reactive. Consequently, initiator is frequently added together with the CTA. In Fig. 4b, the predicted VDF feed rate is compared to experimental data for a case of multiple CTA and initiator shots during the course of the reaction. Despite the increased scatter in experimental data it is clear that the model predictions agree very well with the experimental data.

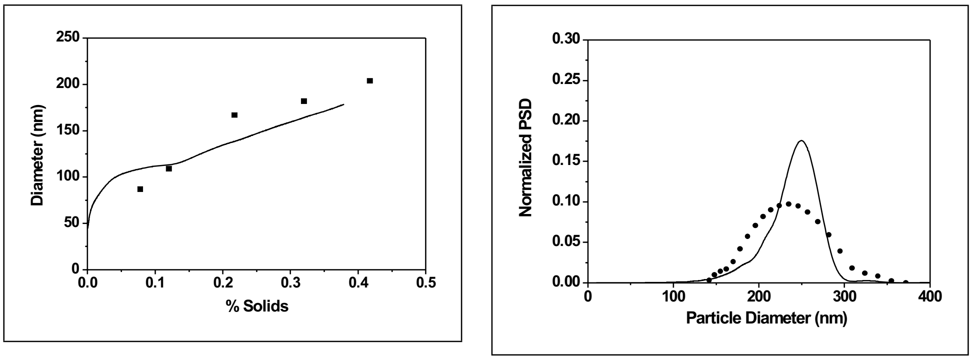

Figure 5. VDF emulsion polymerization (a) Mean diameter (b) Final PSD

In Fig. 5a, the evolution of the mean particle diameter corresponding to the results of Fig. 4a is depicted. In Fig. 5b, the final PSD is shown for the case corresponding to the results of Fig. 2a. As can be seen, the predicted distribution is in fairly good agreement with the experimental PSD. The predicted PSD is slightly narrower but the peak position is accurately predicted to within 15-20nm.

5. Conclusions

A comprehensive mathematical model of the VDF emulsion polymerization process has been developed. The predictives capabilities of the model are demonstrated by a direct comparison of model predictions with experimental data on the rate of monomer consumption, properties of the final latex such as molecular weight distribution and particle size distribution for a VDF emulsion polymerization reactor. It is shown that there is a good agreement between model predictions and experimental data. The rate of monomer conversion depends on both initiator and CTA addition rates during the course of the reaction. The addition of CTA tends to decrease the reaction rate but is counter-balanced by the simultaneous addition to the reactor of an appropriate amount of initiator.

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