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MODELLING AND OPTIMIZATION OF A FED-BATCH EMULSION COPOLYMERIZATION REACTOR OF STYRENE AND BUTYL ACRYLATE IN THE PRESENCE OF A CHAIN TRANSFER AGENT

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Abstract: This paper deals with modelling and optimization of a semi-batch emulsion copolymerization reactor of styrene and butyl acrylate in the presence of n-C12 mercaptan as chain transfer agent (CTA). The model is developed using reaction rate laws available in the literature. The population balance equations are based on a new approach which reduces significantly the number of equations involved and consequently the computation time. The model allows predicting of (i) the global monomer conversion, (ii) the microstructure, the number and weight average molecular weights, and the glass transition temperature of the resulting macromolecules, and (iii) the average particle diameters. A subset of the most influential parameters of the model is identified using a parameter estimability approach.
The resulting model is then validated and used to determine the optimal feed policy which enables to produce core-shell latex particles with a designed glass temperature profile at high conversion. The set of optimal solutions is determined by means of a mutiobjective optimization approach. Finally, the unique solution to be implemented is obtained by using a decision making strategy.

Keywords: modelling, core-shell particles, multiobjective optimization, decision aid

1. INTRODUCTION

Emulsion polymerization is an important industrial process used to produce a large variety of polymers for multiple uses (e.g. paints, adhesives, coatings, varnishes…). Moreover, it has significant advantages over bulk and solution polymerization processes such as heat removal capacity and viscosity control. These advantages result mostly from the multiphase and compartmentalized nature of the emulsion polymerization which allows the production of polymers of high molecular weights with high polymerization rates, delivering a high versatility to product qualities. However, the complexity of emulsion polymerization systems, arising from factors such as the multiphase nature, nonlinear behaviour and sensitivity to disturbances, induces more intense difficulties on modelling and make the development of optimization procedures of emulsion polymerization reactions a very challenging task. Moreover, the production of polymers with specified end-use properties is one of the key issues in polymer industry. The desired end-use properties are usually carried out by using optimization approaches where many and conflicting objective functions are frequently involved. Those problems are referred to as multiobjective optimization problems which are increasingly encountered in chemical processes (Fonteix et al., 2004; Garg and Gupta, 1999; Mitra et al., 2004; Sakar et al., 2007). The optimal solutions are therefore not unique but have sets of non dominated solutions (Pareto's front) which show trade-offs among the whole objectives. A decision making approach is then used to rank Pareto's solutions in order to select the best profiles to be implemented.

This communication deals with experimental investigations, modelling and optimization of a fed-batch emulsion copolymerization reactor of styrene and butyl acrylate in the presence of n-C12 mercaptan as chain transfer

agent. The objective is to optimize the operating variables in order to produce core-shell latex particles with a specific glass transition temperature profile and high conversion rate.

2. PROCESS MODEL

There are many research contributions on modelling emulsion polymerization processes, starting with the conventional Harkins model which identifies three stages: nucleation, particles growth and the end of polymerization. The models available in the literature have different degrees of complexity depending upon their scope and application. The most representative have been reviewed by (Gao and Penlidis, 2002; Chern, 2006; Thickett, 2007).

In this work, a model was developed for batch and fed-batch emulsion copolymerization of styrene and butyl acrylate in the presence of n-C12 mercaptan as chain transfer agent. This model takes into account the main phenomena involved in the process (radical desorption, gel and glass effects, CTA reactions …). Moreover, a new approach has been used to simplify the population balance by using two differential equations instead of a large number of differential equations for the same purpose. This approach reduces the simulation time. On the other hand, the model highlights the effects of the CTA on the molecular weight distributions (MWD) and on the polymerization rates and hence on the monomers conversion.
The model is used to predict different variables including (i) overall monomer conversion, (ii) number and weight average molecular weights and glass transition temperature (T_g) of the resulting macromolecules, and (iii) average particle diameters.
Moreover, an estimability analysis was carried out in order to determine the set of parameters involved in the model which can be identified from the available experimental measurements. The resulting estimable parameters are then identified by minimizing the errors between the prediction and the measured data. The non estimable parameters are obtained from literature. After the parameter identification, the model is validated by means of an additional set of experimental measurements.

3. MULTIOBJECTIVE OPTIMIZATION

The final objective of this work is to produce core-shell particles with specific end-use properties depending on the glass transition temperature profile. The monomers used (styrene and butylacrylate) have different reactivity ratios and the corresponding polymers have very different glass transition temperature (-54 °C for polybutylacrylate and 100 °C for polystyrene). The key feature of the optimisation problem is to determine the optimal feed rate profiles which control the polymerization reactions in order to produce particles with a designed morphology and glass transition temperature.
Two objective functions have been selected for the optimization of this process. The first one is to minimize the error between the glass transition temperature and the desired profile. The second objective is to maximize the final conversion.

$$
\begin{aligned}
&Min\ f = [f_1, f_2] \\
&\quad f_1 = \frac{1}{t_{fc} - t_0}\int_{t_0}^{t_{fc}} \left|T_g - T_{g1}\right| dt + \frac{1}{t_{fs} - t_{fc}}\int_{t_{fc}}^{t_{fs}} \left|T_g - T_{g2}\right| dt \\
&\quad f_2 = -X(t_f) \\
&s.t.\quad \dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x}(t), \boldsymbol{u}(t), \boldsymbol{p}, t)\ ;\ \ x(t_0) = x_0 \\
&\quad \frac{1}{t_{fc} - t_0}\int_{t_0}^{t_{fc}} \left(0.9 - X(t)\right)^2 dt \le \varepsilon^2 \\
&\quad \boldsymbol{u}_{inf} \le \boldsymbol{u}(t) \le \boldsymbol{u}_{sup}
\end{aligned}
$$

where T_g is the glass transition temperature, T_{g1} the desired glass transition temperature for the core, T_{g2} the desired glass transition temperature for the shell, t_{fc} and t_{fs} the times necessary to obtain the corresponding core and the shell respectively, $X(t_f)$ is the final conversion rate at the end of the process and $\boldsymbol{u}$ the control vector (feeds and time periods).
The feed profiles as piece-wise constant and the time periods (Fig.1) which maximize the conversion at the end of the copolymerization process and minimize the difference between the measured and a designed profile of glass transition temperature subject to a set of constraints are determined by means of a multi-objective

optimization approach based on an evolutionary algorithm. The set of non dominated solutions (Pareto's front) was obtained by an evolutionary algorithm. Multiattribute utility theory (MUT) is used as a decision making tool to rank Pareto's solutions and the resulting best solution is implemented within the real system.

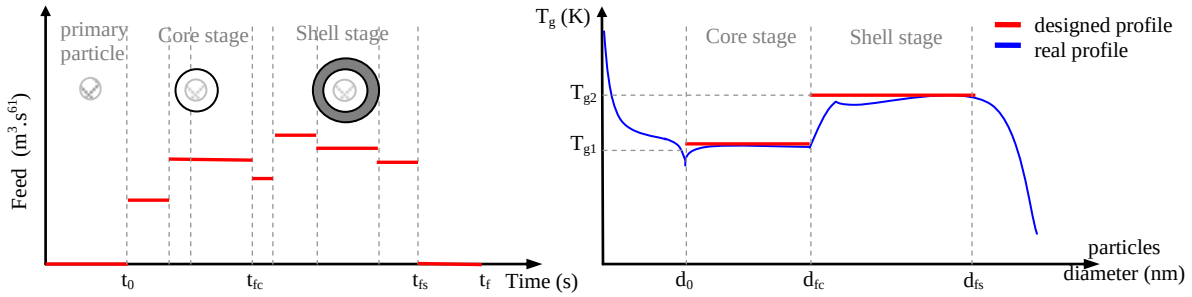

Fig. 1: Optimal feed rates and resulting glass transition temperature profiles

4. CONCLUSIONS

In this work, a dynamic model has been developed and validated for the batch and fed-batch emulsion copolymerization reactor of styrene and butylacrylate in the presence of n-C12 mercaptan as chain transfer agent. This model has then been used in a multiobjective optimization problem designed to determine the optimal feed profiles necessary to produce core-shell latex particles with specific glass transition and high conversion. A decision support approach is used to determine the optimal solution.

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