Control of the morphology of nanoparticles resulting from dynamic optimization of a fed-batch emulsion copolymerization process

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ABSTRACT

This paper deals with the design and control of the morphology of core-shell nanoparticles elaborated by fed-batch emulsion copolymerization of styrene and butyl-acrylate in the presence of a chain transfer agent (n-dodecyl mercaptan). A mathematical model was elaborated and validated. It consists of a system of differential algebraic equations deduced from population balance and involving 49 unknown kinetic and thermodynamic parameters, many of them being impossible to be accurately estimated, due to the lack of experimental data. A method based on the sensitivity analysis allowed us to determine a subset of the 21 most influential parameters. The 28 non estimable parameters were taken from the literature. The model was then used to optimize the best profile of the pre-emulsion feed rate to control (i) the composition and average molar masses of the copolymer, (ii) the instantaneous glass transition temperature, corresponding to a core-shell morphology adapted to special end-use properties.

Keywords: emulsion copolymerization, modeling, dynamic optimization, core-shell nanoparticles, morphology control

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 their multiphase nature, nonlinear behavior and sensitivity to disturbances, induces more intense difficulties on modeling and makes 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 conflicting objective functions are frequently involved. This is known as multiobjective optimization problems increasingly encountered in chemical processes [1-4]. The optimal solutions are therefore not unique but constitute sets of non dominated compromises (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 compromise to be implemented. This communication deals with modeling and dynamic multiobjective optimization of batch and fed-batch emulsion copolymerization of styrene and butyl-acrylate in the presence of a chain transfer agent (CTA): n-dodecyl mercaptan. The objective is to optimize the operating variables in order to produce core-shell particles with a specific glass transition temperature profile and high conversion rate.

2 PROCESS MODEL

There are many research contributions on modeling 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 [5], [6].

2.1 Main assumptions

The establishment of a model requires generally the use of several assumptions to enhance the speed of convergence. In this work, some of these assumptions are made without providing justification, as they are readily accepted and validated in the classical literature. Others which must be given with the necessary explanations are summarized as follows:

- Due to the high surfactant concentration used in this work, only micellar nucleation is considered,
- All reactions in the aqueous phase are neglected except initiation and inhibition,
- The chain transfer agent is subject to diffusional limitations mainly in the droplet-aqueous phase interface,
- The growing particles and the monomer droplets are considered to be monodisperse,
- The reactor is perfectly mixed and isothermal.

2.2 Kinetic Scheme

According to these assumptions, the model is based on the following elementary chemical reactions:
-*in the aqueous phase*: initiation, inhibition, nucleation and radical absorption
-*in the organic phase (particles):* propagation, terminations by combination and disproportionation, inhibition, transfer to monomers, transfer to chain transfer agent and radical desorption.

2.3 Mathematical model

Using this scheme, the development of the kinetic model comprises the writing of reactions rates, mass balance of the various species (initiator, monomers, solvent, CTA, macroradicals and macromolecules), balance of the moments of order 0, 1 and 2 of the degree of polymerization distribution (DPD) of both macroradicals and macromolecules and influence of temperature on kinetic constants. The population balance is based on the assumption that the fraction of particles containing *j* free radicals follows Poisson's law. The model takes also into account the main phenomena involved in the process (radicals desorption, gel and glass effects...). It consists of a system of differential algebraic equations involving 49 parameters to be estimated.

2.4 Parametric identification

A first step, prior to the parameters identification is to evaluate the estimability of these parameters and to determine the subset of potentially estimable. Due to the model structure and possible lack of measurements, the estimation of some parameters appeared to be impossible regardless the amount of available data. The main limitations to the parameters estimability are their weak effect on the measured outputs and the correlation between their effects. Moreover, this estimation can lead to significant degradation in the predictive capability of the model. The development of an effective solution to the parameters selection requires establishing a methodology based on the magnitude of the individual effect of each parameter on the measured outputs [7]. This approach has been applied to the 49 parameters of the model leading to a subset of 21 parameters. The aim of the model was to correctly predict simultaneously the global conversion (X_{ove}), the fraction of residual styrene (Fr_2), the number- and weight-average molecular weights ($\overline{M}_n, \overline{M}_w$) and the average particles diameters (d_p). The model parameters were determined through the minimization of the maximum likelihood criterion, J, with the experimental data.

$$J = \sum_{k=1}^{5} N_k . \ln\left(\sum_{l=1}^{N_k} \left(x_k(t_{kl}) - \hat{x}_k(t_{kl}, \theta) \right)^2 \right) \qquad (1)$$

where N_k is the number of measurements of the variables x_k, t_{kl} is the lth time of measurement of the variable x_k and $\hat{x}_k$ is the value of x_k predicted by the model using the values θ of the unknown parameters. In this relation, the five variables x_k were: X_{ove}, $\overline{M}_n, \overline{M}_w$, d_p and Fr_2.

2.5 Associated results

The measured data were obtained from several batch runs carried out in a 1-liter jacketed reactor, using 1g of initiator, 60 g of styrene, 60g of butyl-acrylate and various CTA concentrations and temperatures [8],[9]. Global conversion, residual monomers, Mn and Mw and Tg were determined by gravimetry, GC using a Delsi Nermag DN 200 chromatograph, SEC using a Waters Millipore equipment, DSC using a Pyris 1 Perkin Elmer apparatus, respectively. Figure 1a shows the time evolution of X_{ove}, for experiments carried out at 60 and 70 °C, each for two different CTA concentrations. As expected, when the temperature is increased the conversion rate is higher. On the other hand, the effect of CTA on the global conversion is quite clear in spite of the weak differences between experimental and simulated values due to the CTA concentrations used in this work. Figure 1b presents the

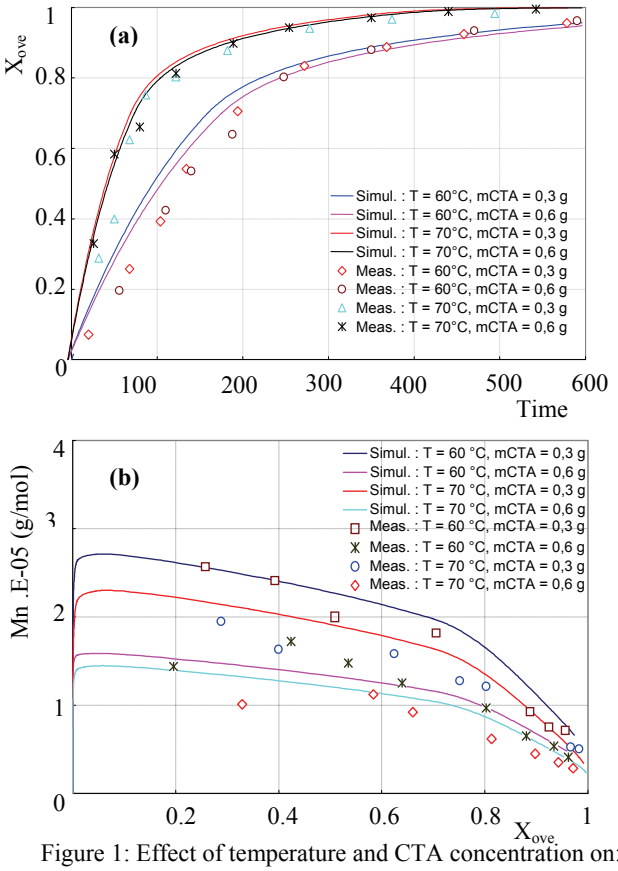

Figure 1: Effect of temperature and CTA concentration on: (a): Overall conversion; (b): Number average molecular weight

evolution of Mn versus X_{ove} for the same runs. As expected, Mn decreases when CTA concentration increases and decreases when the temperature is increased. The same observations were obtained for Mw. On the other hand, smaller particles were produced when the temperature increased. Nevertheless, CTA has a weak effect on the particles average diameters. Moreover, due to the difference between the reactivity ratios of each monomer, styrene is consumed faster than butyl-acrylate and the copolymer composition drifts till the total consumption of styrene. Globally the results show an acceptable agreement between simulated and experimental data.

2.6 Model validation

The model was then validated on new runs realized in batch mode. As shown in the two examples given in figure 2, good agreement was again observed between simulated and experimental data.

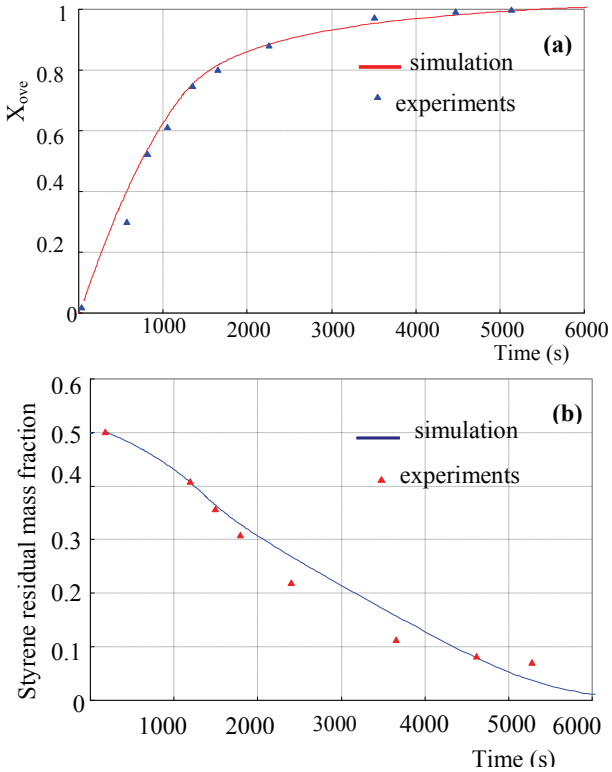

Figure 2: Validation of the model in batch mode:
(a): Overall conversion, (b): Styrene residual mass fraction

The model was also validated with runs carried out in fed-batch mode (figure 3).

3 MULTIOBJECTIVE OPTIMIZATION

The final objective of this work was to produce core-shell particles with specific end-use properties depending on the glass transition temperature profile.

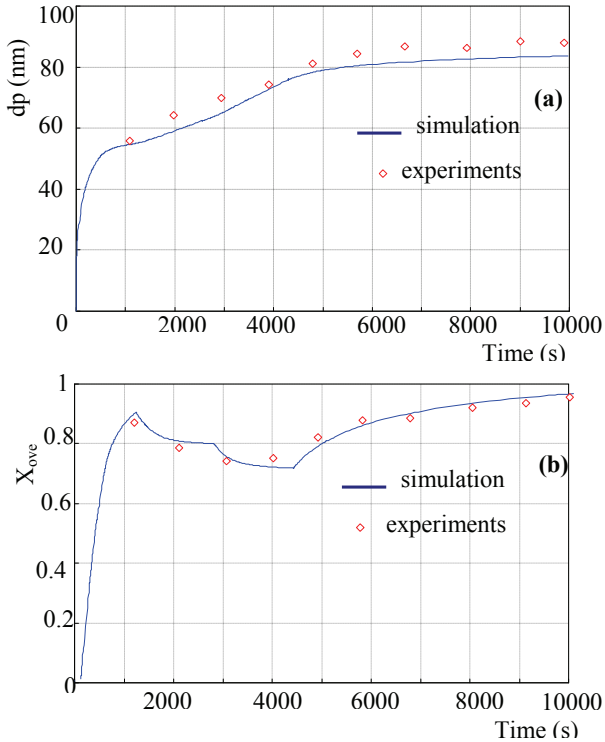

Figure 3: Validation of the model in fed-batch mode:
(a) Average particles diameters,(b) Overall conversion

Considering that the two monomers used have different reactivity ratios and that the corresponding polymers have different Tg (-54°C for PBu and 100 °C for PS), the key feature of the optimization 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, f_1 and f_2, given in equations (2), have been selected for the optimization. The first one aims at minimizing the error between the glass transition temperature and the desired profile, while the second aims at minimizing the final conversion.

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

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 shell

respectively, $X(t_f)$ is the conversion at the end of the process and $\boldsymbol{u}$ the control vector (feeds and time periods).
The feed profiles and the time periods which maximize the conversion at the end of the copolymerization and minimize the difference between the measured and a designed profile of glass transition temperature, were determined by means of a multi-objective optimization approach based on Pareto's approach. The set of non-dominated solutions (Pareto's front), obtained by the use of an evolutionary algorithm [10], is given in figure 4.

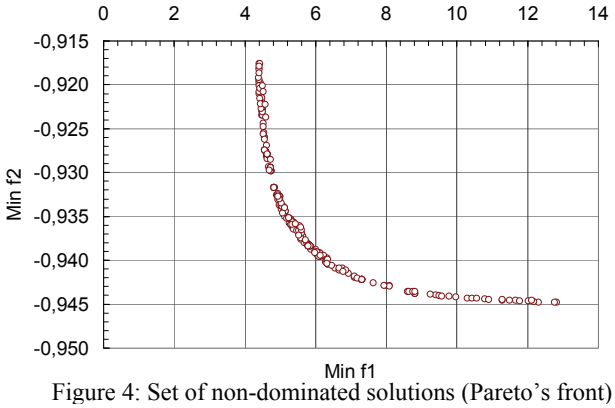

Figure 4: Set of non-dominated solutions (Pareto's front)

Multiattribute utility theory (MAUT) was then used as a decision making tool to rank Pareto's solutions. The resulting best solution implemented within the real system is given in figure 5.

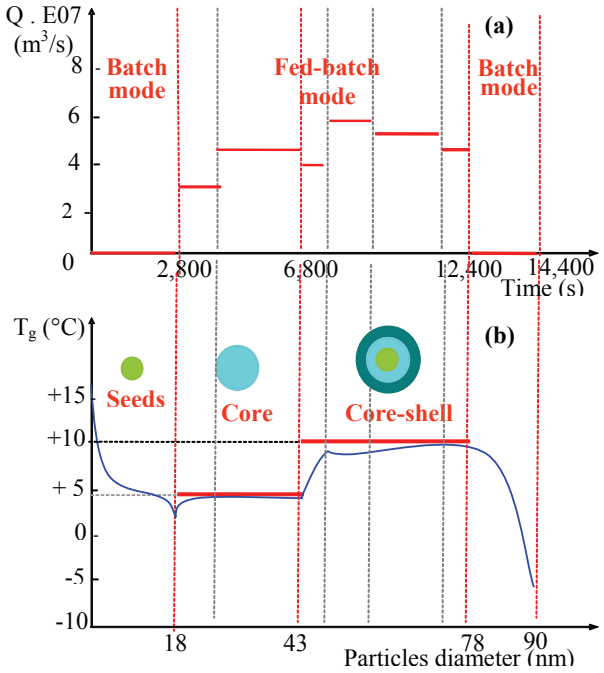

Figure 5: Feed rate (a) and corresponding instantaneous glass transition temperature profiles (b)

4 CONCLUSION

In this work, a dynamic model has been developed and validated for the batch and fed-batch emulsion copolymerization of styrene and butyl-acrylate in the presence of a chain transfer agent (n-dodecyl mercaptan). After its validation, this model has then been used in a multiobjective optimization problem designed to determine the optimal feed profiles necessary to produce, with a high conversion, core-shell latex particles with specific glass transition temperature. A decision support approach was used to determine this optimal solution.

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