

A Chemical Engineering Approach for the Multicriteria Optimization and the Prediction of Latex Properties

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Abstract: Modeling an emulsion polymerization process is of special interest for the prediction of the corresponding latex properties and optimization of several polymer features. A chemical engineering approach is used to elaborate a tendency model, able to predict, with sufficient precision, the conversion, the particles number and polymer properties such as number and weight average molecular weights. This simulation model can be used in a multicriteria optimization procedure to obtain the desired quality of the product with a high productivity. The approach is applied on a well-known system: emulsion polymerization of styrene.

Keywords: Chemical engineering · Emulsion polymerization · Modeling · Multicriteria optimization

1. Introduction

Batch emulsion polymerization is a process well adapted to the production of coatings, inks, adhesives, rubbers, *etc.* The corresponding fundamental mechanisms dictate what will be the properties of the polymer and latex, given particular operating conditions. These properties, like molecular weight distribution or particle size distribution, govern the end-use properties that are important to a customer. So, the objective is to propose a methodology to predict polymer properties from the operating conditions through the elaboration of a simulator.

2. Materials and Methods

A monomer (styrene) emulsion is stabilized by use of an excess of surfactant (sodium dodecyl sulfate) which forms micelles, able to catch free radicals, generated by chain initiator (potassium per-

sulfate). The propagation step needs monomer provided by droplets and free radicals grow in the formed polymer particles. The termination step is controlled by transfer to monomer and by capture of radicals by the particles.

Experimentally, gravimetry is used to determine the conversion while quasi-elastic light scattering and gel permeation chromatography coupled to multi angle laser light scattering are used to determine the particle size distribution and the molecular weight distribution of the macromolecules respectively.

3. Modeling

The model is elaborated to describe all the latex properties by mass balances of all components. From the assumptions of the classical kinetic scheme of emulsion polymerization of styrene, *i.e.* initiation, propagation, transfer to monomer and instantaneous termination, all respective reaction rates are expressed. This model is commonly called the zero-one model (Asua *et al.*, [1]). Sub-models are also elaborated to take into account the particularities of the emulsion polymerization like the nucleation phenomenon, the partition species between all different phases and the viscosity effects (Gilbert, [2]).

The model parameters are determined by parametric identification based on the

maximum likelihood approach (Walter and Pronzato, [3]). The aim is to minimize a function of the square discrepancies between the experimental and the simulated data. The optimal parameters, like the kinetic parameters, are obtained and the model can be used as a simulator to predict the experimental properties (Massebeuf *et al.*, [4]). Finally, the model is able to represent the evolution of conversion, particles number and average molecular weights from different initial concentrations of initiator and surfactant.

4. Optimization

In many optimization problems, we are often confronted with multiobjective decision problems. For example, it makes sense to simultaneously optimize the polymer production and the quality of the product. In our case, we define three criteria: f_1 as a production criterion, f_2 and f_3 as quality criteria.

$$f_1 = X(t_f) \quad (1)$$

$$f_2 = |N_p(t_f) - N_{pd}| \quad (2)$$

$$f_3 = |\bar{M}_w(t_f) - \bar{M}_{wd}| \quad (3)$$

where X is the conversion, N_p the number of particles, \bar{M}_w the weight average molecular weight, t_f the final time of polymerization, N_{pd} and \bar{M}_{wd} the desired values

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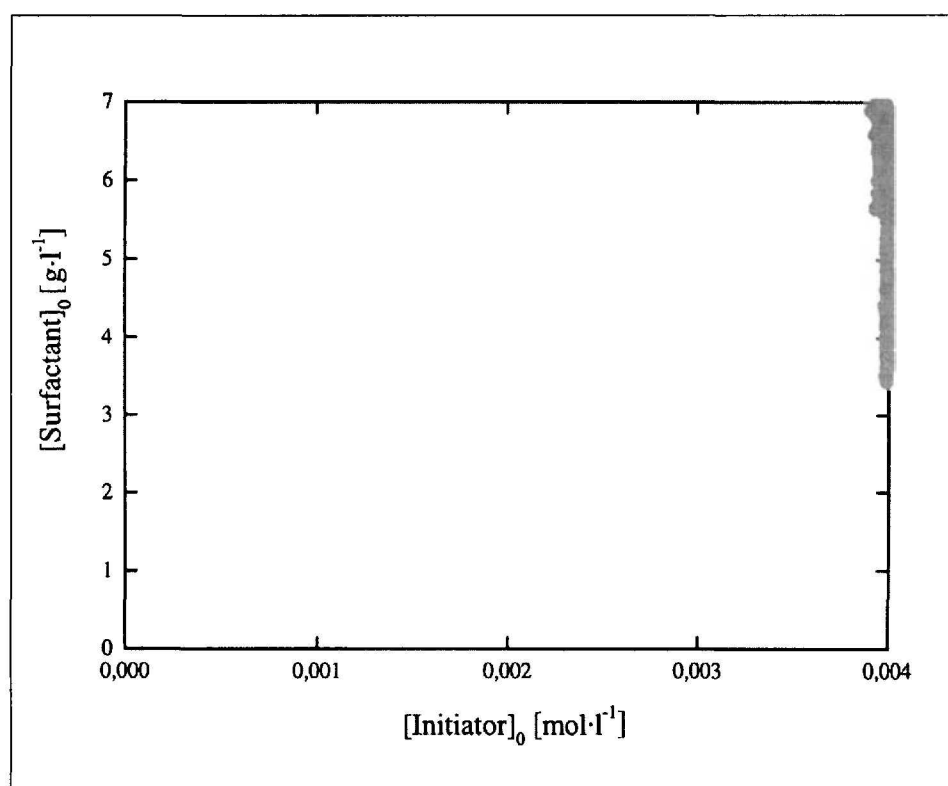


Fig. Pareto set of a batch process of emulsion polymerization of styrene at 60 °C, obtained for initial concentrations of initiator and surfactant.

of the number of particles and of the weight average molecular weight respectively. f_1 has to be maximized and, f_2 and f_3 have to be minimized. The optimal working conditions are not necessarily the same for each objective. A multicriteria optimization procedure is then developed to keep all possible optimal solutions. The domination concept is introduced to obtain a set of optimal solutions called the Pareto set (Fonseca and Fleming, [5]). Two points, in the research domain, are compared. If one is better for all criteria, it is a non-dominating solution. All non-dominating points form the Pareto region.

This procedure is applied on the three criteria for the given values:

$N_{pd} = 5 \cdot 10^{17}$ particles per liter of water, $M_{wd} = 3 \cdot 10^6$ g.mol⁻¹ and $t_f = 3$ hrs. The Pareto set is represented in the Fig. by grey points, for a given reaction temperature: $T = 60$ °C. We can see that the three criteria can be simultaneously optimized for a high quantity of initiator (about 0.004 mol.l⁻¹) and different initial concentrations of surfactants (3.3 to 7 g.l⁻¹). So, this figure gives an initial information about the working conditions to obtain the desired characteristics.

5. Conclusion

A chemical engineering approach has been developed to find the operating conditions which allows multicriteria optimal solutions to be obtained. A model has to be finalized before its use in the whole procedure. From all the solutions of the Pareto set, a decision maker will further have to choose his preferences.

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