17th European Symposium on Computer Aided Process Engineering – ESCAPE17
V. Plesu and P.S. Agachi (Editors)
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Model Based Design of Polymer Product

Dulce C.M. Silva, Nuno M.C. Oliveira

GEPSI - PSE Group, Department of Chemical Engineering, University of Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal. E-mail:{dulce, nuno}@eq.uc.pt

Abstract

This paper describes a methodology for the design of free-radical polymer products based on discontinuous operation. This design problem is characterized by considerable complexity, high dimensionality, nonlinear behavior of the physical models, and multi-objective nature. To avoid most of these limitations, a two-step methodology is introduced, where the problem is initially reformulated in terms of some of the decision variables used. In the second phase, the determination of the remaining complicating variables is completed, from the solution obtained during the previous step. The capability of manufacturing innovative products with improved properties is demonstrated with the batch suspension polymerization of vinyl chloride to produce polyvinyl chloride (PVC), which is one of the currently most widely used thermoplastics.

Keywords: Dynamic optimization, Product design, Polymerization.

1. Introduction

Polymeric materials comprise both high volume commodity products such as plastics, and high quality products with very specific physical properties for tailored applications. The world market for these products is enormous and presents many development opportunities and challenges from a Process Systems Engineering (PSE) perspective. There is considerable potential for improvement of these products, in both cases, which can be done either by adjusting the physical properties of the existing products to the application demands, or through the design of new products, which extend the applicability of solutions based on polymeric materials. This is possible because of the huge

impact that the molecular and morphologic properties have on the physical properties of the final products, and consequently on their feasible end-uses.
Very detailed and precise mechanistic kinetic models for the manufacture of several polymer products are becoming available in the literature, at least for the most common reaction schemes and products. At a more macroscopic level, this information can be combined with experiments designed to elucidate the influence of the processing conditions on the physical structure of the final product. Hence the development of systematic strategies for the optimal design of these products is extremely welcome, to put into good use all of this information available.
Previous efforts related to the optimization of polymer products have considered mostly productivity improvements resulting from minimum time formulations [1], or the effects of constraining the variance of the chain length distribution of the final product [2]. Besides these concerns, other aspects need also to be considered, in a versatile approach, for a successful product design approach:

1. Accurate control of the size distributions (moments and general shape).
2. Complete choice of operating conditions (such as temperature, concentrations) and processing agents, such as suitable initiators (which ones, how many, in which concentrations, when to add), and other additives like suspension or chain transfer agents.

In the end, the resulting design problem is almost invariably characterized by its considerable complexity and multi-objective nature, due to the size, complexity and highly nonlinear behavior of the physical models, and the need to perform discrete design decisions. This explains why this type of problems has received, so far, little attention in the specialized literature.
This work introduces a sequential methodology for the design of free-radical based discontinuous polymer products, where the above aspects can be explicitly considered.

2. Problem formulation and solution strategy

We consider the problem of optimally obtaining a polymeric material with given molecular characteristics, or a material that maximizes a performance criterion that can be expressed in terms of these molecular properties. The design problem can be generally formulated as a discrete optimal control of the form

$$\begin{aligned} \min_{\substack{\theta, z, u(t)\in H_i,\\ x(t), y(t)\in H_o}} \quad & \Psi(\bullet) \\ \text{s.t.} \quad & \dot{x} = f_p(x,u,z;\theta), \quad y = g_p(x;\theta), \quad h(u,z) \le 0 \\ & u_l \le u \le u_u, \quad x_l \le x \le x_u, \quad y_l \le y \le y_u, \quad z \equiv \{z_j, j \in D\}, \quad z_j \in \{0,1\} \end{aligned} \tag{1}$$

Here $\Psi \equiv \{\psi_i, i \in F\}$ is a set of given objective functions, and H_i is a subset of the problem time horizon $H_o \equiv \{t \mid t \in [0, t_F]\}$, where t_F represents the duration of the operation. The process model is represented by the f_p and g_p functions, which are assumed to be differentiable and continuous, except perhaps at a finite number of switching points, introduced for instance by the discrete variables z. These variables are used to express the choice of (perhaps optional) processing agents, such as initiators. The state variables are denoted by $x \in \mathbf{R}^{n_s}$, $u \in \mathbf{R}^{n_i}$ are the input variables, $\theta \in \mathbf{R}^{n_p}$ are the system parameters, and $y \in \mathbf{R}^{n_o}$ is the output vector. h is used to express the logical constraints between the discrete and continuous decision variables, and can be assumed to be linear. Each objective ψ_i can be expressed in terms of the state and output variables during the time interval H_o or, more frequently, at the end of the problem horizon. A typical example is

$$\psi_i(\bullet) = (y_{\mathrm{F}} - y_{\mathrm{sp}})^{\mathrm{T}} Q (y_{\mathrm{F}} - y_{\mathrm{sp}})$$

where y_{sp} represents desired final property values, y_{F} is the set of output variables at the end of the run, and Q is a weighting matrix. This corresponds to formulating the design problem using soft constraints, since the set of initial product specifications might not be completely feasible. Another example is the use of

$$\psi_i(\bullet) = \int_0^\infty W_F(r)(r - \bar{r})^2 \, dr$$

where r is the chain length, $\bar{r}$ is the average chain length and $W_F(r)$ is the polymer weight fraction with chain length r, at the end of the operation. This corresponds to the direct minimization of the variance of the product distribution, in order to obtain a product with more uniform properties.

A first step towards the solution of (1) is the parameterization or discretization of the continuous variables $u(t), x(t), y(t)$. This can be done by choosing one of the existing frameworks for solution of dynamic optimization problems [3]. In our case, a sequential methodology is used, where only $u(t)$ is discretized, assuming piecewise constant values inside each sampling interval [2]. After this reformulation, we obtain a differentially constrained MINLP, which is generally difficult to solve, given the model characteristics described before. Therefore, we consider a sequential solution of the original problem, using different sets of decision variables, in two phases.

2.1. First phase - Optimization of the specified molecular properties

Since the existence of discrete decision variables in (1) constitutes one of the major solution difficulties, we consider a reformulated optimization problem, during the first solution phase. For processing agents such as initiators, instead of deciding which ones should be used, and when, something that requires

making discrete decisions, we consider alternatively the optimal (continuous) profile of the overall initiation rate, as an equivalent continuous decision variable for the first phase. Together with the remaining degrees of freedom corresponding to the profiles of physical variables $u(t)$ (such as temperature) during the operation, this allows the formulation of a standard nonlinear dynamic optimization problem, of the form:

$$\begin{aligned} \min_{\theta, v\in H_{ik}, x, y} \quad & \Psi(\bullet) \\ \text{s.t.} \quad & \dot{x} = f(x, v; \theta),\ \ y = g(x; \theta) \\ & v_l \le v \le v_u,\quad x_l \le x \le x_u,\quad y_l \le y \le y_u \end{aligned} \tag{2}$$

Here $v \equiv \{v_k, k \in I\}$ represents the set of discretized input variables $u(t)$ in (1), together with the initiation rates $\bar{R}_{\mathrm{I,k}}$ for each discretization interval k, which are also assumed to remain piecewise constant. This constitutes a good approximation of the original system behaviour, provided that small sampling intervals are used.

The multiobjective nature of (2) is then considered, using one of the known reformulation techniques to a standard NLP [4]. This is an important aspect in polymer product design, since many problems have complementary aspects, better described by different performance indexes. The solution of (2) determines then how well it was possible to achieve each individual goal, without degrading the remaining ones. It provides us with the optimal initiator rate $\bar{R}_{\mathrm{Iopt},k}$, together with the profiles for the continuous variables of the system.

2.2. Second phase - Selection of appropriate processing agents

In the second phase, we need to select the initiators (their type, number and concentration) suitable for the set of objectives considered previously, together with their respective addition policies. Distinct goals are also considered in this phase: the relative cost of each agent, the quality of the approximation to the desired initiation rate profile obtained in the previous step, and the residual level of initiators at the end of the operation. The problem can be formulated as:

$$\min_{z_i, I_{0,i}, Q_{j,i}} \quad \sum_{i=1}^{N_{\mathrm{I}}} c_i Q_{\mathrm{t},i} \tag{3}$$

$$\text{s.t.} \quad \bar{R}_{\mathrm{I},k} = 2\sum_{i=1}^{N_{\mathrm{I}}} f_i k_{di,k} I_{ik}, \quad |\bar{R}_{\mathrm{I},j} - \bar{R}_{\mathrm{Iopt},k}| / |\bar{R}_{\mathrm{Iopt},k}| \le \varepsilon \tag{4}$$

$$Q_{\mathrm{t},i} = I_{0,\mathrm{i}} + \sum_{k=1}^{n} Q_{i,k} T, \quad I_{ik} = \varphi_{0k} I_{0,i} + \sum_{j=1}^{k} \varphi_{1j} Q_{ij}, \quad I_{\mathrm{R}} \le \varepsilon_R \tag{5}$$

$$z_i m \le Q_{\mathrm{t},i} \le z_i M, \quad \sum_{i=1}^{N_{\mathrm{I}}} z_i \le N_{\mathrm{I,max}} \tag{6}$$

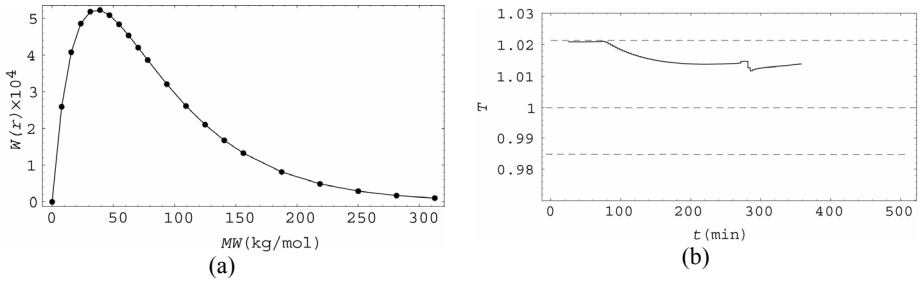
$$Q_{i,k} \ge 0, \quad I_{0,\mathrm{i}} \ge 0, \quad z_i \in \{0,1\}, \quad i = 1, \cdots N_1; k = 1, \cdots n \tag{7}$$

Here, $I_{0,i}$ and $Q_{\mathrm{t},i}$ define the total amount of initiator i added at the beginning and during the operation, respectively, and z_i is a binary variable that indicates

whether initiator i is added during the polymerization. The amount of the initiator i should be non-zero if this initiator is present in the mixture; M and m represent the upper and lower limits imposed on the initiator amounts, respectively. The maximum allowed amount of initiators present at the end of the operation, I_R, is controlled by the parameter ε_R. The maximum number of allowed initiators, $N_{I,max}$, to be added during the polymerization process is defined by (6). The quality of the initiation rate fit is defined by (4). Here a maximum error is controlled by the parameter ε. $\overline{R}_{\mathbf{Iopt},k}$ is the desired value for the initiation rate at the instant k, i.e. the value which is obtained from the solution of (2), in the previous phase. The cost of the initiators added during the polymerization (c_i) is taken into consideration in the objective function.
To solve the previous optimization problem a relation between the initiation rate and the concentration of the initiators present in the mixture along the operation is necessary. The expression derived in (5) is linear with respect to $I_{0,i}$ and $Q_{i,k}$, and the coefficients can be computed given the initiation rate and temperature profiles determined before. This leads to a MILP problem for the selection of initiators, which can be easily solved with available numerical software.

3. Optimization Results

Because of its high production volume and low cost, the PVC polymer constitutes a natural candidate for the application of tools for polymer design with improved properties. In this work, a detailed model was built based on the kinetic information of [5] and molecular weight distribution (MWD) taken from [6]. Since the molecular properties are highly correlated with the physical properties, the goal in this example is to find optimal profiles for producing a polymer with the MWD represented in Fig. 1(a) by the solid line.



(a) (b)

Figure 1: (a) Final PVC polymer molecular weight distribution and (b) the normalized optimal profile of the temperature polymerization (• obtained; — desired).

In this case, temperature constraints of $50^{\circ}\mathrm{C} < T < 62^{\circ}\mathrm{C}$ were enforced. Fig. 1(b) shows the optimal temperature profile obtained. As it can be observed from Fig. 1(a), the MWD obtained closely matches the desired one. Table 1 shows the recipe used to obtain the reference PVC polymer in Fig. 1(a), and the results obtained through optimization. The most rapid initiator of the list (`i17`) is

added at the beginning and also during the operation (see Fig. 2), while the initiator `i14` is added only at the beginning of the operation. Significant reductions on the total amount of initiators to be added during the operation and on the total cost are obtained, when compared with the base case. As lower quantities of initiators are added during the operation and more rapid initiators are selected, lower residual initiator levels are also predicted, which is quite advantageous.

Table 1: Comparison of initiator policies and respective cost.

Case	Selected initiators	Total cost ($\times 10^3$ m.u./kg VCM)	Amount added ($\times 10^3$ mol/kg VCM)	Residual amount ($\times 10^3$ mol/kg VCM)
Base	`i12, i13`	3.93	1.77	5.96
Optimal	`i14, i17`	1.19	1.46	3.29
Reduction (%)		**69.7**	**17.6**	**44.7**

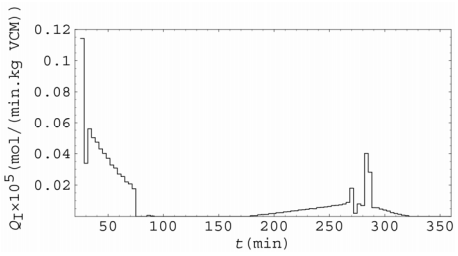


Figure 2: Optimal feed rate of the initiator `i17`.

4. Conclusions

A methodology to avoid some of the difficulties associated to the design of free-radical based discontinuous polymer was presented in this paper. This was successfully applied to the batch suspension polymerization of vinyl chloride in order to manufacture innovative products with improved properties.

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