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Assessing optimal growth of desired species in epoxy polymerization under uncertainty

Kishalay Mitra*

Research & Development, Engineering and Industrial Services, Tata Consultancy Services Limited, Quadra II, Survey Number 238/239, Magarpatta, Hadapsar, Pune 411028, Maharashtra, India

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ABSTRACT

While carrying out optimization studies on kinetic scheme based models of polymerization reactions, there are kinetic parameters that need to be tuned with process data during model building exercise and henceforth assumed constant during the entire course of optimization studies. As these parameters are subjected to experimental and regression errors, some levels of uncertainty are embedded in them. Hence, handling them as constant parameters and thereby neglecting the uncertainty associated with them during the entire course of optimization is not realistic. These problems are handled formally in the paradigm of optimization under uncertainty where uncertainty propagation of these parameters through model equations is reflected in terms of system constraints and objectives that facilitate a designer to unveil the tradeoff between solution optimality and robustness. Chance constrained fuzzy simulation based approach is one such methodology that merges the facets of chance constrained programming and fuzzy logic and is adopted here to carry out an analysis in determining optimal performance of a semi-batch epoxy polymerization reactor under uncertainty in kinetic parameters used for model building. The aim of this study is to find out the tradeoff among optimal growth of the desired species, solution robustness and productivity achieved through optimal discrete addition rates of different ingredients, e.g. bisphenol-A, epichlorohydrin and sodium hydroxide while maintaining the constraints on the control variables that are expressed in terms of bounds on M_n, PDI and other constraints reflecting the experimental conditions realistically. The deterministic multiobjective optimization model of Majumdar et al. [11] forms the basis of this work on which various effects of uncertain parameters are shown and analyzed in a Pareto fashion using real coded fuzzy chance constrained NSGA II.

1. Introduction

Epoxies, the thermosetting resins that contain one or more reactive epoxide groups in the uncured form, have a wide range of applications. The chemistry of epoxies not only allows curing process to produce polymers with a very broad range of properties such as adhesion, chemical and heat resistance, good mechanical and electrical insulating properties but also helps imparting new properties into epoxies through different ways, e.g. silver-filled epoxies can show good electrical conductivity as opposed to their inherent insulating properties [1]. Among many, few important applications of epoxy are in coatings, general purpose adhesives, fiber-reinforced plastic materials, industrial tooling. The non-hazardous epoxy coatings that can provide a tough, UV resistant, protective coating with excellent hardness and abrasion resistance are developed for heavy duty service on metal substrates and have edge over heat-cured powder coatings in terms of less energy consumption. The high performance epoxy adhesives that have advantage in heat and chemical resistance over other common adhesives are used in the construction of aircraft, automobiles, and other applications where high strength bonds are required. Industrial tooling applications like molds, laminates, castings, fixtures, etc., are produced using epoxies as a replacement for metal or similar other traditional materials, to improve the efficiency, lower the overall cost or shorten the lead-time for many industrial processes. Epoxy is used as a structural matrix material in aerospace industry which is then reinforced by fiber. Other applications range in electrical systems, composites, art, aerospace, wind energy, consumer and marine applications, etc. [1]. It is, therefore, not surprising that the field of epoxy polymerization has drawn a significant attention of the polymer industry in the past few decades.

Epoxies are most popularly produced by Taffy process [2] where the monomer, bisphenol-A (AA_0) is reacted with excess epichlorohydrin (EP) in the presence of sodium hydroxide (NaOH) to form polymer that has a glycidyl ether end groups (building block) at both the ends. Advancement process [3] is the other route where

* Tel.: +91 20 66224711; fax: +91 20 66224499.
E-mail addresses: kishalay.mitra@gmail.com, kishalay.mitra@tcs.com.

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Nomenclature

AA_0	bisphenol-A (monomer)
B	sodium phenoxide end group
EP	epichlorohydrin
f	objective function in optimization problem
g_i	ith constraint in optimization problem
HSS	Hammersley sequence sampling
k_i	reaction rate constant (i = 1, 2, 3,4, 5)
l_iEE_n	ith moment of EE species
M_n	number average molecular weight
M_w	weight average molecular weight
NaOH	sodium hydroxide
N	sampling size in fuzzy simulation
N_{max}	maximum number of generations in NSGA II
N_{pop}	population size in NSGA II
p_c	crossover probability in NSGA II
p_m	mutation probability in NSGA II
Pr	probability measure
Pos	probability measure
PDI	polydispersity index (M_w/M_n)
PO	Pareto optimal
r_i	fuzzy numbers
s_i	fuzzy sets
u_i	ingredient addition amounts for different ingredients at different time points (i = 1, 2, . . ., 21)
$\mathbf{U}_i(t)$	ingredient profiles comprising seven ingredient addition amounts (u_i) at seven equidistant ($t_{sim}/7$) time points (i = 1, 2, 3 for NaOH, EP and AA_0, respectively); ($\mathbf{U}_1(t) = [u_1, u_2, \ldots, u_7]^T$, $\mathbf{U}_2(t) = [u_8, u_9, \ldots, u_{14}]^T$, $\mathbf{U}_3(t) = [u_{15}, u_{16}, \ldots, u_{21}]^T$)
x	decision variable set
λ_i	ith moment (here i = 0, 1, 2)
γ_1	objective function 1 which is ratio of concentration of species EE_0 and sum of the concentration of all other nine species
γ_2	objective function 2 which is the ratio of first and zero order moments for species EE_0
ξ	set of uncertain fuzzy parameters
α_i, β_i	premeditated confidence levels to the respective constraints

Subscripts and superscripts

max	upper bound for constraint on PDI
min	lower bound for constraint on M_n
$\tilde{m}$	denoting the parameter m is uncertain
$\hat{m}$	denoting a particular realization of uncertain parameter m

pulverized NaOH is added in steps to the reaction mixture of AA_0 and EP dissolved in a solvent. It is established that alkali has a key role in epoxy polymerization and is added in semi-batch mode [4]. Progress in the study of modeling and optimization of industrial epoxy polymerization reactors is very rare in literature to the best of the knowledge of the author. Batzer and Zahir [5] conducted experiments on an isothermal epoxy batch reactor and provided data for evolution of concentration of oligomeric species with respect to processing time. Raha and Gupta [6] carried out a modeling exercise on similar isothermal epoxy batch reactor based on species balance and equation of moment approach and presented a corresponding validation of results on the same experimental data provided by Batzer and Zahir [5]. They estimated the kinetic parameters from available experimental data through an optimization exercise. Raha et al. [7] extended this work to the semi-batch operation of the epoxy reactor, where the effect of discrete addition amounts of NaOH during the entire processing time is thoroughly studied (AA_0 and EP added in batch mode only). In this multiobjective optimization work, simultaneous maximization of the number average molecular weight (M_n) and minimization of the polydispersity index (PDI) for a targeted product quality was studied. Initial low caustic addition followed by high additions in the later stages led to high M_n and low PDI. Long processing time is recommended to stabilize the product composition due to the intermittent depletion of some unstable species. In a subsequent work, Deb et al. [8] identified different addition patterns for all three ingredients (NaOH, EP and AA_0) in a semi-batch epoxy reactor for a very broad range of lower to higher molecular weight polymer molecules while achieving maximization of M_n, minimization of PDI and minimization of processing time, simultaneously. Though this study shows how basic theory of multiobjective optimization can be implemented in a complex (non convex) problem in a generic way and some salient operating principles of optimal epoxy operation can be unveiled through multiobjective optimization study, this study largely undermines some relevant process issues. Mitra et al. [9,10] modified the earlier study of Deb et al. [8] with more practical optimization objectives, and relevant constraints in two subsequent studies where the maximization of selective species were discussed and constraints that help an optimization exercise to remain close to available experimental conditions (Batzer and Zahir [5]) to avoid any kind of extrapolation errors were incorporated. As compared to maximizing M_n and minimizing PDI (reflecting average properties), maximizing growth of desired species along with the formation of its lower oligomers found to be a better objective set in the study of Mitra et al. [9] where a three-objective optimization, minimizing the total NaOH additions being the third objective, is carried out with a hope of having a better control over the evolution of some desired species. It also became clear that the semi-batch mode of operations is superior to the batch mode for all practical purposes. In the other work of Mitra et al. [10], focus has been given to extract the optimal addition histories of the reactants for having a polymer with the maximum M_n processed in minimum processing time with the polydispersity index within a given range. Both the approaches, i.e. hourly addition approach and equal interval strategy were tried, but frequent additions arising from the latter approach might face limiting conditions from mass and heat transfer aspects. Subsequently, Majumdar et al. [11] considered few more relevant objectives such as minimization of possible by-products, minimization of the overall product stabilization time, etc., in addition to minimization of total amount of NaOH addition, maximization of desired species concentration and its lower chain propagation and found out the Pareto solutions and their corresponding ingredient addition patterns for running the epoxy reactor optimally.

Most of the multiobjective optimal control studies cited above are based on the assumption that the kinetic model parameters of the system under consideration are known with complete certainty. These kinetic parameters are estimated by an optimization exercise where these parameters are varied within permissible bounds to minimize the square of the error between the experimental data and model predictions for some model attributes (oligomeric species concentration in this case). As these parameters are tuned with process data and subjected to experimental and regression errors, some levels of uncertainty are embedded in them. Hence, handling them as constant parameters and thereby neglecting the uncertainty associated with them is not realistic. These problems are handled formally in the paradigm of optimization under uncertainty where uncertainty propagation of these parameters through model equations is reflected in terms of system constraints and objectives that facilitate a designer to unveil the tradeoff between solution optimality and robustness [12–15].