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Assessing optimal growth of desired species in epoxy polymerization under uncertainty

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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

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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].

Stochastic programming, chance constrained programming and fuzzy mathematical programming [12] are different methodologies for handling optimization problems under uncertainty based on the pioneering work of Beale [16], Bellman [17], Bellman and Zadeh [18], Charnes and Cooper [19] and Dantzig [20].

In stochastic programming, several scenarios of realizations of uncertain parameter are assumed and propagation of the effect of parameter uncertainty is attained through expectation calculation of objective functions and constraints over all those premeditated realizations of uncertain parameters [21]. Here the assumption is that the probability distributions governing the uncertain parameters are either known or can be estimated from the exiting data. Applications of this approach in handling uncertainty in process system engineering literature are found in large numbers [22–31]. Exponential increase in problem size with the increase in the number of uncertain parameters is one of the drawbacks of this approach. Chance constrained programming [19,32–34] requires feasibility of solutions with at least some probability specified on constraints having uncertain parameters, expressed in terms of reliability of the solution as opposed to stochastic programming that requires decisions have to be feasible for all the outcomes of uncertain parameters. The main advantage of chance constrained programming technique lies in the ability to control the size of the deterministic equivalent problem even if the number of uncertain parameters is large. Applications of CCP in process system engineering literature are few in number [35–38]. On the other hand, fuzzy mathematical programming, proliferated by Zimmermann [39], neither assumes that the uncertain parameters have to follow any statistical distribution nor allows the final deterministic equivalent formulation of the uncertain model to blow up in size with increase in number of uncertain parameters. Here, a mathematical model is formulated taking into account the decision maker's expectations of a target range of the objective values and soft constraints while making decisions in a fuzzy environment. In this approach, the degree of satisfaction of a constraint is defined in terms of a membership function of the constraint and a small extent of constraint violation is allowed. Application of FMP is widely spread across different applications such as capacity planning [40] supply chain planning [41], production scheduling [42], bio-energy production [43], etc., to name a few.

In this paper, we consider the more realistic scenarios of handling uncertainty in model parameters that are otherwise assumed constant during the entire course of optimization such as kinetic parameters and explore the merits of fuzzy chance constrained programming towards analyzing their impact on the overall optimization of the epoxy polymer processing system. Multiobjective optimization of the epoxy polymerization system is carried out with an aim of productivity maximization and evolution of desired species under kinetic parameter uncertainty and the results are analyzed in Pareto sense. This needs treatment of uncertainty propagation in constraints as well as one of the objectives that is tackled here using a fuzzy simulation based chance constrained programming approach. To the best of the knowledge of the author, such analysis has not been considered in earlier work of polymer literature. The techniques for handling optimization under uncertainty for nonlinear systems are rare though their counterparts for linear models are available in literature. It is, therefore, no exception that these techniques are not applied to polymer systems earlier since polymer models are extremely nonlinear in nature. The deterministic multiobjective epoxy polymerization of Majumdar et al. [11] forms the basis of this work on which various impacts of uncertainty have been analyzed. Real coded nondominated sorting genetic algorithm, NSGA II, a popular elitist evolutionary multiobjective optimization approach, is used for solving the multiobjective optimization under uncertainty. The rest of the paper is organized as follows: first, a brief overview of the process model is described. In subsequent subsections, optimization formulation under uncertainty followed by a note on possibility calculation is provided. Results of epoxy polymerization system under uncertainty are presented in Section 3 in detail. Finally the work is summarized and concluding remarks are provided.

2. Model and problem formulation

2.1. Model

The kinetic scheme considered for the epoxy polymerization system is taken from the work of Raha and co-workers [6,7]. They have used this scheme to build their kinetic model and validate with experimental data of oligomeric species provided by Batzer and Zahir [4]. Ordinary differential equations (ODEs) are derived for various species using species balance and method of moment approach [6]. These set of ODEs are integrated using explicit Runge–Kutta (RK) type numerical routines and kinetic parameters assumed in the scheme are estimated with the help of error minimization kind of optimization exercise. There are 48 state variables that are used to describe various system "states" ($\mathbf{x}=[x_1, x_2, \ldots, x_{48}]^T$) including all species balance and moment balance equations as follows:

$$\frac{dx_i}{dt} = f_i(\mathbf{x}, \mathbf{U}); \quad i = 1, 2, \ldots, 48 \tag{1}$$

where $\mathbf{x}$ and $\mathbf{U}$ ($=[\mathbf{U}_1(t), \mathbf{U}_2(t), \mathbf{U}_3(t)]^T$) are the vectors of the state and manipulated variables (intermediate addition amounts of NaOH [$\mathbf{U}_1(t)$], EP [$\mathbf{U}_2(t)$] and AA_0 [$\mathbf{U}_3(t)$] at different times), respectively. Details on the various molecular species including the monomer considered for the modeling exercise can be found in the published article of Raha et al. [7]. Given discrete addition amounts at different times for three ingredients ($\mathbf{U}$ at time zero and other time steps) and initial values of all state variables ($\mathbf{x}$ at time zero), the reaction scheme model can be integrated to a prespecified polymer processing time (t_{sim}). This simulation package is combined with real coded nondominated sorting genetic algorithm (NSGA II) [44,45] to perform stochastic multiobjective optimization exercises (defined in next few sections). Though the multiobjective optimization problem described in this work could have been solved by many other methods mentioned available in the literature [46], the rationale behind choosing NSGA II for this study is based on its excellent performance on various studies conducted by the research group of the author in the past [46]. Details on NSGA II are omitted here for the sake of conciseness and inquisitive readers can refer literature [45] for that.

2.2. Multiobjective optimization under uncertainty

The deterministic multiobjective optimization problem considered here is taken from the first case study of Majumdar et al. [11]. Details on this formulation are not repeated here for the sake of brevity and can be found in the work of Majumdar et al. [11]. There are five kinetic parameters (k_1, k_2, k_3, k_4 and k_5) corresponding to the assumed polymerization reaction. These parameters are treated as constants in the deterministic formulation. As they are subjected to uncertainty, the optimization under uncertainty formulation takes their effect into consideration. These parameters are assumed uncertain because most of them are obtained from the regression of experimental data and thus are subject to uncertainty due to regression and experimental errors. Considering that the probability distributions of these uncertain parameters are often not easy to obtain and, therefore, not available, we assume these uncertain parameters as fuzzy numbers and intend to treat the optimization under uncertainty using a combined approach of fuzzy mathematical programming and chance constrained programming [47–49]. The deterministic multiobjective optimization

problem [11] can now be converted into the equivalent stochastic multiobjective optimization formulation under the fuzzy chance constrained programming paradigm as follows:

Objectives

$$\max_{u_i, t_{sim}} \bar{\gamma}_1$$
$$\min_{u_i, t_{sim}} \bar{t}_{sim}$$
$$\min_{u_i, t_{sim}} \bar{\gamma}_2$$

Subject to constraints

$$\mathrm{Pos}(\tilde{\gamma}_1(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \geq \bar{\gamma}_1) \geq \beta_1$$
$$\mathrm{Pos}(\tilde{t}_{sim}(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq \bar{t}_{sim}) \geq \beta_2$$
$$\mathrm{Pos}(\tilde{\gamma}_2(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq \bar{\gamma}_2) \geq \beta_3$$
$$\mathrm{Pos}(\tilde{P}DI(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq \mathrm{PDI}^{max}) \geq \beta_4$$
$$\mathrm{Pos}(\tilde{M}_n(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \geq M_n^{min}) \geq \beta_5$$
$$\mathrm{Pos}\left(\left(\frac{[\tilde{E}P](\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)}{[\tilde{N}aOH](\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)}\right)_t \geq 3.0\right) \geq \beta_6$$
$$\tilde{\gamma}_1 = \frac{\tilde{\lambda}_0^{EE}(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)}{\sum_j \tilde{\lambda}_0^j(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)}$$
$$\tilde{\gamma}_2 = \frac{\tilde{\lambda}_1^{EE}(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)}{\tilde{\lambda}_0^{EE}(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)}$$

All model equations [6,7]

$i = 1, \ldots, 21$
j = AA, AB, AE, AF, BB, BE, BF, EE, EF, FF

Constraints for manipulated variables

$$\sum_{i=1}^{7} u_i \leq 1.0 \quad \text{(for NaOH)}$$
$$\sum_{i=8}^{14} u_i \leq 3.0 \quad \text{(for EP)}$$
$$\sum_{i=15}^{21} u_i \leq 1.0 \quad \text{(for } AA_0\text{)}$$

Manipulated variable bounds

$$\begin{aligned} &0.1 \leq u_1 \leq 1.0; \quad 0.0 \leq u_i \leq 1.0 \quad (i = 2, 3, \ldots, 7) \\ &0.1 \leq u_8 \leq 2.0; \quad 0.0 \leq u_i \leq 2.0 \quad (i = 9, 10, \ldots, 14) \\ &0.1 \leq u_{15} \leq 1.0; \quad 0.0 \leq u_i \leq 1.0 \quad (i = 16, 17, \ldots, 21) \end{aligned} \tag{2}$$

Constraints and all the objectives affected by these uncertain parameters are expressed in terms of possibility of getting satisfied with a premeditated level of β_i. Three auxiliary variables $(\bar{\gamma}_1, \bar{t}_{sim}, \bar{\gamma}_2)$ are introduced here to handle three fuzzy objectives that have uncertain parameters. The above formulation is not easily solvable due to the presence of uncertain parameters, probability and possibility measures. Hence, the deterministic equivalent of the same has to be defined. It is known that the results for obtaining the deterministic equivalent for only some specific linear cases are available [47,48] and the same for complicated nonlinear cases are usually hard to achieve. Liu and Iwamura [47,48] suggested the concept of fuzzy simulation for calculating probability of satisfying constraints for nonlinear cases. This will be described in the next section.

Table 1
Pseudo-code for possibility calculation of a constraint with a premeditated confidence level β_4, e.g. $\mathrm{Pos}(\tilde{P}DI(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq 1.61) \geq \beta_4$.

Step	Procedure
1	Assume Pos = 0
2	From the β_4 cut set of the fuzzy parameters $(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)$, generate a particular realization (denoted as $\hat{k}_1, \hat{k}_2, \hat{k}_3, \hat{k}_4, \hat{k}_5$) uniformly
3	Compute the PDI ($\hat{P}DI$) through model simulation for the particular realization $(\hat{k}_1, \hat{k}_2, \hat{k}_3, \hat{k}_4, \hat{k}_5)$ of uncertain parameters
4	Calculate $\mu = \min\{\mu_{k_1}(\hat{k}_1), \mu_{k_2}(\hat{k}_2), \mu_{k_3}(\hat{k}_3), \mu_{k_4}(\hat{k}_4), \mu_{k_5}(\hat{k}_5)\}$, the membership function, if $\hat{P}DI \leq 1.61$
5	Update Pos = μ, if $\mu >$ Pos
6	Repeat steps 2–5 for premeditated number of simulation runs (say, N)
7	Stop simulation if the premeditated number of simulation runs is reached and return Pos

Remark: If the β_4 level set of the fuzzy vector is difficult to determine, it is suggested [47,48] to sample a vector $(\hat{k}_1, \hat{k}_2, \hat{k}_3, \hat{k}_4, \hat{k}_5)$ from the hypercube containing the β_4 level set and accept or reject it based on $\mu(\hat{k}_1, \hat{k}_2, \hat{k}_3, \hat{k}_4, \hat{k}_5) \geq \beta_4$ or not. In order to speed up the simulation process, the hypercube should be designed as small as possible.

Table 2
Pseudo-code for possibility calculation of an objective with a premeditated confidence level β_2, e.g. $\mathrm{Pos}(\tilde{t}_{sim}(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq \bar{t}_{sim}) \geq \beta_2$.

Step	Procedure
1	Assume $\bar{t}_{sim} = \infty$ (in our case this is virtually a large value)
2	From the β_2 cut set of the fuzzy parameters $(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5)$, generate a particular realization (denoted as $\hat{k}_1, \hat{k}_2, \hat{k}_3, \hat{k}_4, \hat{k}_5$) uniformly
3	Select the processing time ($\hat{t}_{sim}$) by optimization routine for the particular realization $(\hat{k}_1, \hat{k}_2, \hat{k}_3, \hat{k}_4, \hat{k}_5)$ of uncertain parameters
4	Update $\bar{t}_{sim} = \hat{t}_{sim}$, if $\hat{t}_{sim} < \bar{t}_{sim}$
5	Repeat steps 2–4 for premeditated number of simulation runs (say, N)
6	Stop simulation if the premeditated number of simulation runs is reached and return $\bar{t}_{sim}$

2.3. Possibility calculation

Two scenarios are going to be discussed here that will be used for the calculation of possibilities of constraints and objectives in fuzzy simulation:

(i) Calculation of possibility of a constraint with a premeditated confidence level β_4, e.g. $\mathrm{Pos}(\tilde{P}DI(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq \mathrm{PDI}^{max}) \geq \beta_4$ (see Table 1 for detailed flow of calculation).
(ii) Calculation of possibility of an objective with a premeditated confidence level β_2, e.g. $\mathrm{Pos}(\tilde{t}_{sim}(\tilde{k}_1, \tilde{k}_2, \tilde{k}_3, \tilde{k}_4, \tilde{k}_5) \leq \bar{t}_{sim}) \geq \beta_2$ (see Table 2 for detailed flow of calculation).

Diwekar and Kalagnanam [50] have proposed a new quasi-random sampling technique, namely Hammersley sequence sampling (HSS) that has been shown to exhibit better homogeneity property over the multivariate parameter space, is used here. Further, the rapid convergence property of HSS over its other counterparts (Monte Carlo sampling or Latin hypercube sampling) suggests that relatively precise estimates of possibility calculation can be achieved by taking a relatively smaller sample size.

2.4. NSGA II parameter settings

Each solution is represented as a real-valued vector of 22 manipulated variables (7 addition amounts for each of three NaOH, EP, AA_0 and a single value of t_{sim}) in NSGA II. Using these values, the

constraints and objectives are calculated by means of fuzzy simulation of epoxy polymerization model. SBX, the simulated binary crossover and the polynomial mutation operators [44] are used as genetic operators to create new solutions. Elitist nondominated sorting is used to identify different Pareto fronts in the merged population of parents and children. The variable bounds are not allowed to be violated due to the adaptation of two strategies on NSGA II, e.g. (i) solutions are initially created within the specified lower and upper bounds, and (ii) if the new solutions go out of these bounds, they are forced to be on the corresponding bounds. Constraints are handled by constrained tournament selection operator [44]. In this, two of the candidate solutions are randomly picked and compared. These solutions can be either feasible or infeasible. If both of them are infeasible, one with lesser constraint violation is selected. For both of them being feasible, either the one with better non-constraint-dominated set wins if they belong to different non-constraint-dominated sets or the one that resides in less crowded area wins if they belong to the same non-constraint-dominated set. A feasible solution of course wins over an infeasible solution when compared. Different schemes of Pareto ranking and density estimator [45] along with this selection operation create a selection pressure for the algorithm to converge as close to the true PO solutions as possible and maintain as diverse a population as possible [44]. When a premeditated maximum iteration count (N_{max}) is reached, NSGA II is terminated and the nondominated solutions of the final population are declared as the obtained PO solutions. Values for different parameters used in NSGA II for this study are: $N_{max} = 150$; a population size of $N_{pop} = 100$; crossover and mutation probabilities of $p_c = 0.9$ and $p_m = 0.01$; distribution index for SBX operator = 0.01; distribution index for the polynomial mutation operator = 0.01; sampling size in fuzzy simulation = 500. Each optimization procedure is initiated with 10 different initial populations to build a confidence on the obtained optimized solutions. Starting with initial population that are randomly generated in the given search field, NSGA II converges to the final PO solutions at around 100–120 generations and able to maintain the solutions till the N_{max} number of generations.

3. Results and discussion

The physics based model used here is tuned with the data provided by Batzer and Zahir [5] which can be found from our earlier work [11] and not presented here for the sake of conciseness. One of the aims to analyze the multiobjective optimization problem under uncertainty considered here is to show the effect of uncertainty involved in the kinetic parameters on the Pareto optimal (PO) front. The three dimensional PO front for the optimization under uncertainty formulation given in Eq. (2) is presented in Fig. 1. The three objectives considered here do not have a straight forward relationship among them. For example, the ratio of EE_n and sum of the other species concentration (i.e. objective 1) has a tradeoff with processing time (objective 2) because higher value of objective 1 is possible with higher value of processing time and we wish to maximize the first objective and minimize the second objective. Similarly, objective 1 and objective 3 have tradeoff relationship because we wish to maximize the objective 1 and minimize the objective 3 simultaneously whereas higher value of objective 1 is feasible with higher value of objective 3. On the other hand, processing time has a favorable relationship with the objective of chain propagation (objective 3) as low chain propagation values are available with lower processing time and we want to minimize both of them simultaneously. Considering all three objectives together, we can see the aforementioned tradeoff again as shown in Fig. 1.

While considering the uncertainty problem, all data are kept same as the deterministic multiobjective optimization first case

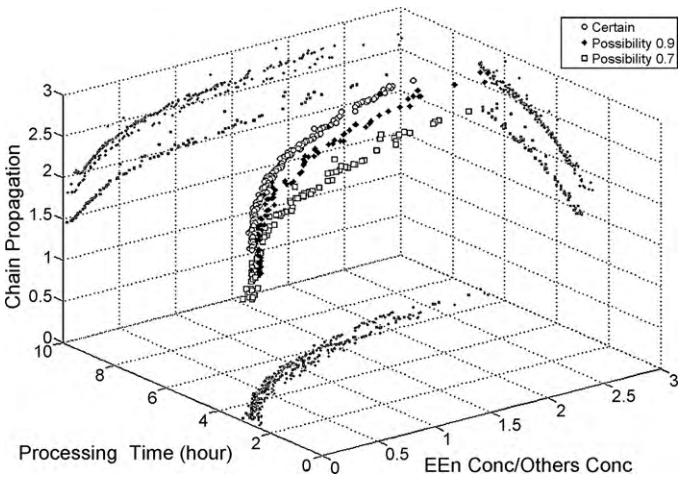

Fig. 1. Multiobjective Pareto optimal solutions for different levels of uncertainty.

study [11] except the uncertain parameters. Often, the information on any distribution on these kinetic parameters is not available. We, therefore, assume these uncertain parameters as fuzzy parameters and represent their uncertain behavior in terms of triangular fuzzy membership functions. Tip of the triangle (middle point) being lying at the same value of the deterministic case and an allowance of 90% is provided on both sides of the triangular membership function. The effect of parameter uncertainty on the PO fronts is shown in Fig. 1. Due to the complicated tradeoff among various objectives as mentioned above, we intend to analyze the effect of uncertain parameters on PO fronts on three two-dimensional planes (planes of objectives 1–2, objectives 2–3 and objectives 1–3, respectively). Concentrating on the objective 1–3 plane (plane of "EE_n Conc/Others Conc" vs. "Chain Propagation"), we can clearly identify the tradeoff between solution optimality and robustness. Probability of a constraint getting satisfied in chance constrained programming which is treated in the form of possibility in fuzzy chance constrained programming is a measure of reliability or robustness of the obtained solution [35,37]. The PO fronts become better as we move in the order "certain" → "possibility 0.9" → "possibility 0.7". However, the solution becomes less and less reliable gradually in this direction. This means that the solution reliability deteriorates in the direction of better PO fronts. However, we aim to have better PO fronts with maximum solution reliability. Here lies the tradeoff. Appearance of this reliability adds another dimension to the three dimensional Pareto plot in Fig. 1. We can further infer from this that as the possibility value increases, many of the solutions that were feasible for lower values of possibility become infeasible and search space for optimization shrinks leading to relatively inferior PO fronts.

Another standard practice in industry is to replace the uncertain parameters with their nominal values to handle situation under uncertainty when the distribution information for uncertain parameters is available. Qualitatively, we see the similar situation for the triangular fuzzy membership function as we see for normal distribution where the distribution is more concentrated near the nominal value and the intensity reduces gradually on either sides of it. In these cases, if we assume the nominal value to coincide with the tip of triangular fuzzy membership function, which is true in our case, we can say that the process run using the nominal values of the uncertain parameters could have missed to materialize the full opportunity of the problem because it is shown here that by relaxing the uncertain parameters from their crisp values used in deterministic optimization, better PO front can be achieved in the objective 1–3 plane. This has been shown also in some of the other work by the group of the author [37,41]. Fig. 1 further

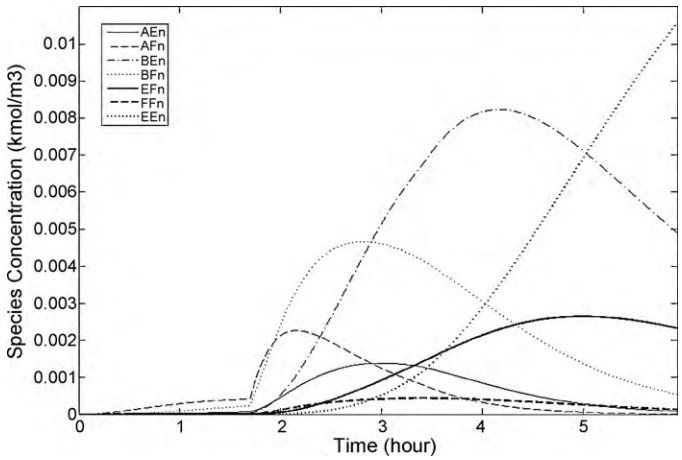

Fig. 2. Temporal growth of various species for a PO solution taken from the PO set given in Fig. 1.

shows how optimization in the presence of parameter uncertainty presents significantly different results in terms of PO fronts. Similar tradeoff among other objectives and reliability in the objective 2–3 plane is also visible. Here also we can see that the nature of PO points gets better with reduction in possibility value. However, this aspect is visible in the objective 1–2 plane to some extent (compare the cases "certain" and "Possibility 0.9"), while distinction between the cases "Possibility 0.9" and "Possibility 0.7" are not as clear as it is in case of other two two-dimensional aforementioned planes. Since objective 2, objective 3 and reliability show a tradeoff among them, we can see the tradeoff among all four objectives (maximization of reliability can be a fourth objective), in Fig. 1. However, it is relatively easy to comprehend the situation when the objective space is confined to two dimensions as it is shown in another case study of industrial grinding [49]. From the PO solutions in Fig. 1, it is visible that better solutions can be achieved by sacrificing some amount of reliability in obtained solutions. Comparing the "Certain" case and the case of "Possibility 0.7" in Fig. 1, we investigate the extent of improvement in each of these objectives keeping one of the objectives fixed. If we keep the processing time fixed (at a value of 5 h), there is a scope of 32% improvement possible in the objective 1 and around 19% improvement in the objective 3. Similarly, keeping the objective 1 fixed (∼1.5), around 3% and 20% improvement can be experienced in processing time and objective 3, respectively. These improvements are possible at the cost of some reliability of the obtained solutions. As we move from the "certain" case to the case of "Possibility 0.7", we lessen the control over the uncertain constraints to the extent of the expressed possibility value whereas for the "certain" case, we do not allow the constraint to be violated at all. We, therefore, can realize that this kind of study on uncertain parameters shows the effect of being less stringent in terms of constraint satisfaction on objectives and clearly demonstrates the corresponding improvement in solution optimality at the cost of solution reliability. One of the PO solutions from Fig. 1 for the possibility value 0.9 is presented in the form of species distribution in Fig. 2 which shows how with the present formulation, species

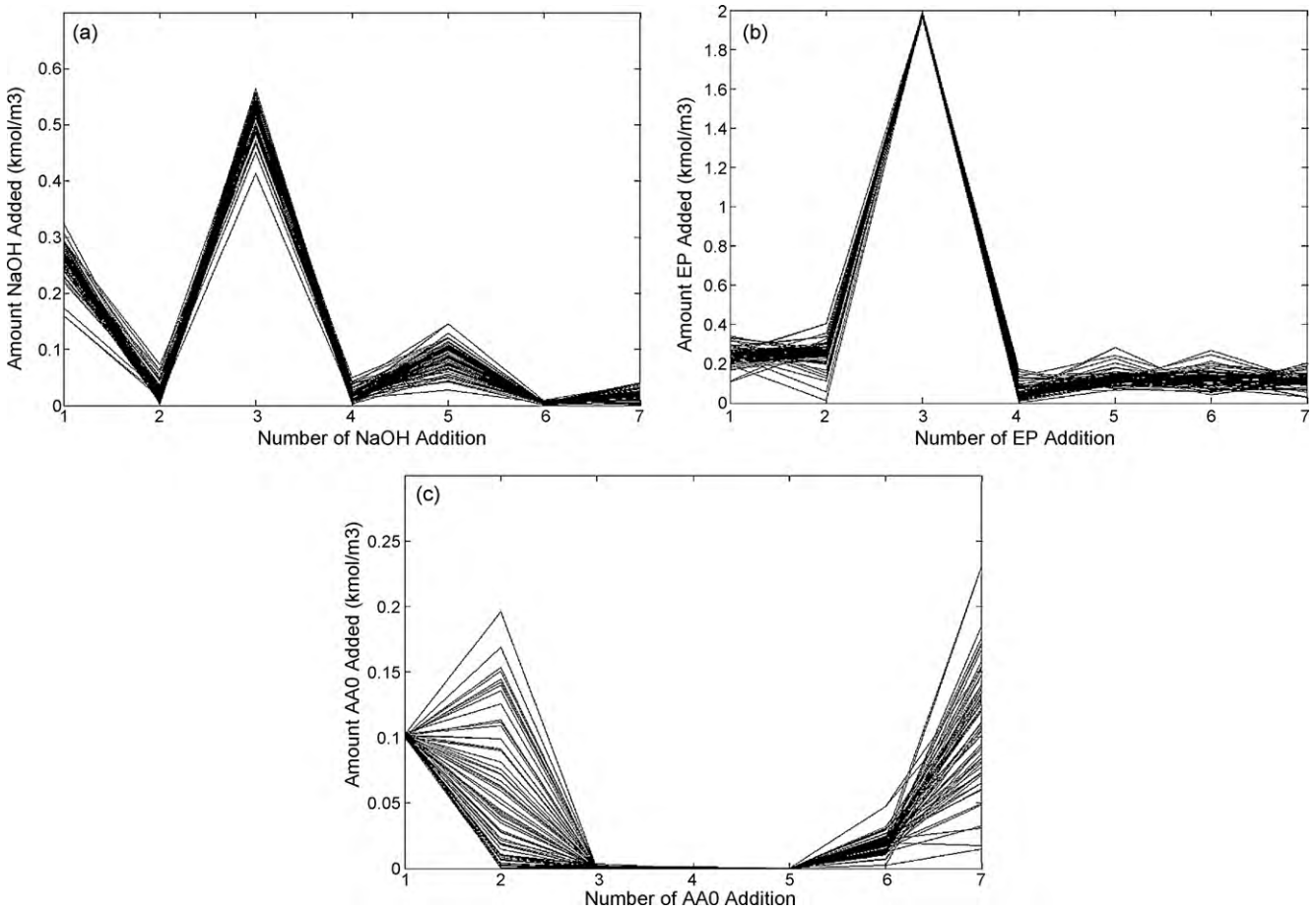

Fig. 3. (a) Similarity of $\mathbf{U}_1(t)$ profiles, i.e. NaOH addition amounts $u_1, u_2, \ldots, u_7$ among PO solutions presented in Fig. 1 for possibility level 0.9; (b) similarity of $\mathbf{U}_2(t)$ profiles, i.e. EP addition amounts $u_8, u_9, \ldots, u_{14}$ among PO solutions presented in Fig. 1 for possibility level 0.9 and (c) similarity of $\mathbf{U}_3(t)$ profiles, i.e. AA_0 addition amounts $u_{15}, u_{16}, \ldots, u_{21}$ among PO solutions presented in Fig. 1 for possibility level 0.9.

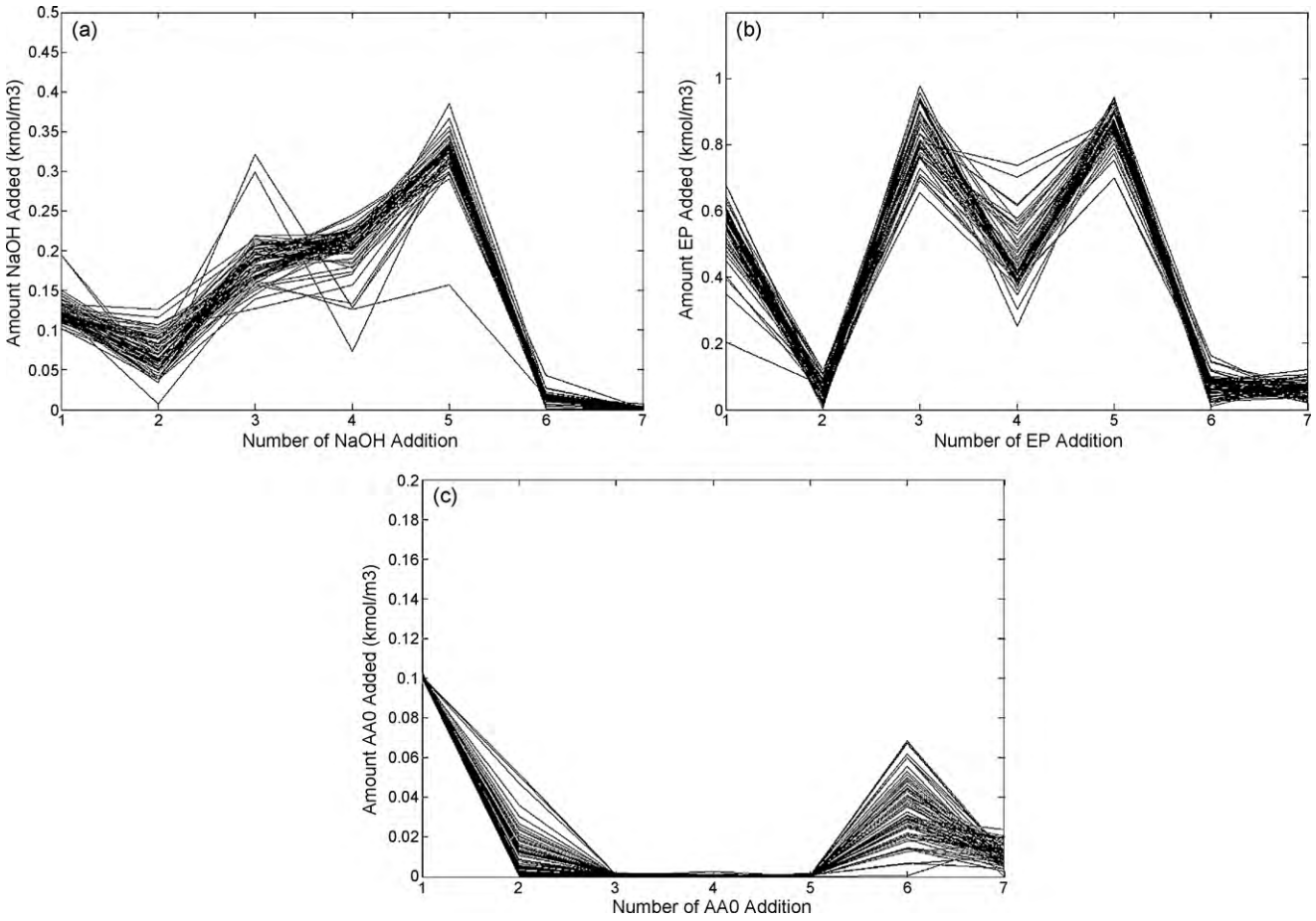

Fig. 4. (a) Similarity of $\mathbf{U}_1(t)$ profiles, i.e. NaOH addition amounts $u_1, u_2, \ldots, u_7$ among PO solutions presented in Fig. 1 for possibility level 0.7; (b) similarity of $\mathbf{U}_2(t)$ profiles, i.e. EP addition amounts $u_8, u_9, \ldots, u_{14}$ among PO solutions presented in Fig. 1 for possibility level 0.7 and (c) similarity of $\mathbf{U}_3(t)$ profiles, i.e. AA_0 addition amounts $u_{15}, u_{16}, \ldots, u_{21}$ among PO solutions presented in Fig. 1 for possibility level 0.7.

concentration of EE_n can grow with concentration of other species reducing down towards the end of the polymer processing time which was the objective for this study. Though a single solution is required to implement in real life problems, a large number of alternatives is provided for an operator by this study and the final selection of the solution is purely based on the requirement of the operator, i.e. the operator can give relatively more or less importance to different objectives and converge to a solution based on the requirement.

Next we investigate whether similarity exists among profiles of manipulated variables for PO points within same possibility value, i.e. whether $\mathbf{U}_1(t)$, $\mathbf{U}_2(t)$, $\mathbf{U}_3(t)$ of different PO points of possibility 0.9 have some similarities in nature. Similar thing can be investigated for PO points of possibility 0.7 as well. The Fritz–John necessary conditions for Pareto optimal solutions [44,51] indicating that there exist a number of mathematical conditions which every Pareto optimal solution must satisfy lead to believe if the obtained solutions are close to the PO solutions will share some similarities among them [52,53]. For PO points corresponding to possibility 0.9 in Fig. 1, we can plot $\mathbf{U}_1(t)$, $\mathbf{U}_2(t)$ and $\mathbf{U}_3(t)$ where y-axis is the amount of addition for respective ingredients and x-axis is the seven ingredient added at different equidistant time points (e.g. $\mathbf{U}_1(t)$ plot consists seven different manipulated variables of u_1, $u_2, \ldots, u_7$ in x-axis with their values in y-axis). Fig. 3(a)–(c) shows the profiles for NaOH, EP and AA_0, respectively. These ingredient addition amounts, though discrete in nature, are added with lines to show the trends among them. From the trends, it is evident that AA_0 along with NaOH is very critical to initiate the reaction process followed by the presence of EP and NaOH that form unstable species which further depletes with time to form the desired polymer species. More amount of EP ensures epoxy groups present in both ends leading to EE_n formation. Fig. 4(a)–(c) shows the similar curve for possibility value 0.7. Comparing the corresponding trends with the same of possibility value 0.9, one can say that in this case, starting amount of NaOH addition is relatively less which is followed by more additions in the subsequent steps. Trends for EP are different in terms of more frequent addition of relatively less amount. Trends for AA_0 are quite same except in case of possibility 0.7, the amounts of additions are less. The corresponding control variable (M_n, PDI) values with processing time as third dimension are shown in Fig. 5 for the case of deterministic as well as possibility values of 0.9 and 0.7. Given a set of objectives, certain trends emerge from the system can be termed as the "blue print" of the system because this information directly talks about what should be the set points of the concerned manipulated variables to drive the system towards optimality. Further, these similarities corroborate the Fritz John criteria mentioned earlier. Such observation has also been observed in other engineering design problems such as gearbox design, truss-structure design, etc. [52], and in other chemical process optimization problems, such as in deterministic multiobjective optimization of various processes like epoxy polymerization [8,11], industrial grinding [53], iron ore sintering process [54], continuous casting process [55], Poly-propylene terephthalate (PPT) polymerization [56], iron ore induration [57]. Various rules of these types can be used as innovative and intelligent thumb rules and practiced by process

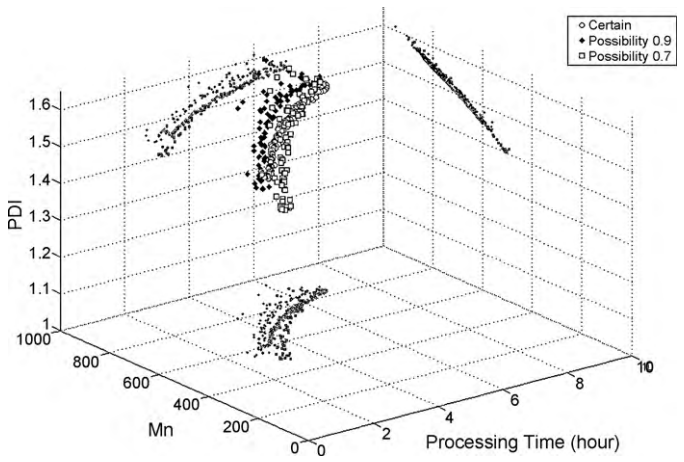

Fig. 5. Values of M_n and PDI for Pareto optimal solutions presented in Fig. 1 for different levels of possibility values.

engineers to improve the operation of epoxy polymerization system.

This kind of study on optimization under uncertainty can be immensely beneficial for a process under operation. One of the differences between stochastic and deterministic optimization is the ability to address the trade off between solution quality (optimality) and reliability in case of stochastic optimization. Better optimal solution can be achieved by sacrificing the reliability attached with the solution. Once this tradeoff is obtained, there could be various PO fronts based on the different reliability levels. Next, the higher level information has to be provided to determine the exact extent of reliability that the enterprise can assume based on its existing risk apatite. Fixing this reliability level means a particular PO front has been fixed for an operator. Now, based on the similar figures presented in Figs. 3 and 4 corresponding to fixed reliability level, the operator knows how to run the reactor towards achieving the optimal performance. Figs. 3 and 4 are nothing but the operators' principle to run the plant optimally or near optimally and they are arrived at by the multiobjective methodology mentioned above.

4. Conclusion

Multiobjective optimization of an epoxy polymerization system under kinetic parameter uncertainties is studied in this work. Maximization of a selective species in the presence of other undesired species, in a species balance based kinetic model, is achieved along with simultaneous consideration of minimization of processing time and minimization of chain propagation. An uncertainty framework amalgamating the concept of chance constrained programming and fuzzy mathematical programming is proposed that makes use of the deterministic multiobjective optimization model of Majumdar et al. [11] and results are analyzed in Pareto fashion in the backdrop of the deterministic formulation. The systematic study of the uncertainty analysis for parameters that are otherwise assumed constant during the course of optimization has not only shown the scope of improvement as compared to the deterministic optimization problem, but also demonstrates the tradeoff between the solution optimality and reliability.

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