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Optimized species growth in epoxy polymerization with real-coded NSGA-II

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Abstract

Satisfaction of twin objectives of maximization of M_n along with minimization of PDI do not necessarily guarantee the maximization of concentration of desired species in a semibatch epoxy polymerization process. As the final product consists of a number of polymer species, a need is felt to perform an advanced optimization study to come up with such process conditions for which the selective growth of a particular polymer species is maximized in minimum possible processing time and the population of other species should be at their lowest values. These above-mentioned conflicting objectives frame the platform for a multi-objective optimization problem, which is solved here using a real-coded non-dominated sorting genetic algorithm or NSGA II and Pareto optimal solutions are obtained. The decision variables are discrete addition rates of various ingredients, e.g. the amount of addition of bisphenol-A (a monomer), sodium hydroxide and epichlorohydrin at different time steps. All species balance equations, bounds on M_n, PDI and addition amounts are treated as constraints. Results are very promising in terms of optimized operations for selective enhancement of desired polymer species for the epoxy polymerization process. Total additions are kept very close to available experimental conditions to minimize probable extrapolation errors. It has been observed that preferential oligomer production is extremely difficult for epoxy polymerization. Lower chain polymers are the only choice for a good quality, stable polymer product.

Keywords: Epoxy; Selective growth; Kinetics

1. Introduction

Epoxies are used by the plastics industry in many ways. One of the examples is in combination with glass fibers (i.e. impregnating fibers with liquid epoxy resins) to produce high-strength composites or reinforced plastics that provide higher strength, electrical and chemical properties, and heat resistance. Typical uses for epoxy-glass reinforced plastics are in aircraft components, filament wound rocket motor casings for missiles, pipes, tanks, pressure vessels and tooling jigs and fixtures. Epoxies are also used in the encapsulation or casting of various electrical and electronic components and in the powder coating of metal substrates. Major outlets for epoxies also include adhesives, protective coatings in appliances, industrial equipment, gymnasium floors, etc. and sealant. Epoxies are thermosetting resins that, in the uncured form, contain one or more reactive epoxide groups.

In Taffy process [1], the most popular industrial process for preparing epoxy polymers, bisphenol-A (AA_0), a monomer, and epichlorohydrin (EP), in excess, are reacted in the presence of sodium hydroxide (NaOH) leading to polymer formation that has a glycidyl ether end group (building block) at both the ends. In the other route, advancement process [2], pulverized sodium hydroxide is added in steps to the reaction mixture of bisphenol-A and epichlorohydrin dissolved in a solvent. It is well established that in all commonly used industrial processes of epoxy polymerization, alkali has a key role, which is usually added in semi-batch mode. Alkali controls oligomeric impurities in the advancement process [1,3].

Experimental and theoretical studies are very few in open literatures for the epoxy polymerization process. Batzer and Zahir [4] conducted experiments on an isothermal batch reactor for epoxy polymerization and provided data for oligomeric species concentration with processing time. Studies on optimization of epoxy reactors are also very rare according to the knowledge of the authors. Raha and Gupta [5] used species balance and equation of moment approach to study the batch process. Raha et al. [6] extended this work with a detailed simulation study about the effect of different addition amounts

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Nomenclature

AA_0	bisphenol-A (monomer)
AE_n	molecular species defined in Table 2
B	sodium phenoxide end group
EP	epichlorohydrin
k_i	reaction rate constant
M_n	number average molecular weight
M_w	weight average molecular weight
NaOH	sodium hydroxide
PDI	poly-dispersity index (M_w/M_n)
λ_i	*i*th moment (here $i=0$, 1, 2)
liEEn	*i*th moment of EE species

and patterns over the performance of the process in semi-batch fashion. They have estimated the kinetic parameters from available experimental data through a simple genetic algorithm (SGA). Raha et al. [7] also examined the effect of NaOH on the pareto optimal (PO) solutions while simultaneously maximizing the number average molecular weight (M_n) and minimizing the polydispersity index (PDI) for a targeted product quality, amount of added NaOH at different time steps being the decision variables. Optimum NaOH addition profiles is identified and demonstrated through case studies. Caustic addition, low initially followed by high in the later stages, leads to high M_n and low PDI. Due to the intermittent depletion of some unstable species, long processing time is recommended to stabilize the product composition.

An elaborate optimization study for epoxy polymerization has been performed by Deb and co-workers [8]. This study performs three gross optimization problems: (a) maximization of M_n with minimization of PDI, (b) maximization of M_n with minimization of processing time and (c) maximization of M_n, minimization of PDI with minimization of processing time. They have identified different addition patterns for all three reactants for lower to higher molecular weight growths. Though this study is an elaborate optimization study and describes how basic theory of optimization can be implemented in a complex problem in a generic way, this study largely undermines some relevant process issues. Two subsequent detailed studies by Mitra et al. [9,10] have modified the earlier study of Deb et al. [8] with more practical optimization objectives, and relevant constraints. These studies for the first time discuss the selective species maximization. Another important feature is the constraints for additions, which remain close to available experimental conditions (Batzer and Zahir [4]) to avoid any kind of extrapolation error from the process conditions for which the model is tuned. In the study of Mitra et al. [9], though the primary aim was to extract the addition patterns of the reagents for maximum M_n with minimum PDI simultaneously, growth of specific species along with the preferential formation of lower oligomers came out to be better objectives as M_n and PDI can only reflect the average properties for the epoxy process. Three-objective optimization with the additional objective of minimizing the total NaOH additions produces a set of choices to the operator, from where one can choose appropriate operating conditions using proper engineering judgements without sacrificing the product quality much. Different species distributions and their evolutions with time have been studied. It has also become clear that the semi-batch mode of operations for the epoxy processes is supposed to be superior to the one-time addition processes (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 number averaged molecular weight processed in minimum possible time with the polydispersity index within a given range. Different product distributions and their formations with time have been studied. Sensitivity analysis has been done for the estimated kinetic parameters to see their probable effects over the process performances. Optimized addition patterns lead to quicker stabilization of product composition. The hourly addition approach can be changed to an equal interval strategy (keeping the same number of additions), but frequent additions may face limiting conditions from mass and heat transfer aspects.

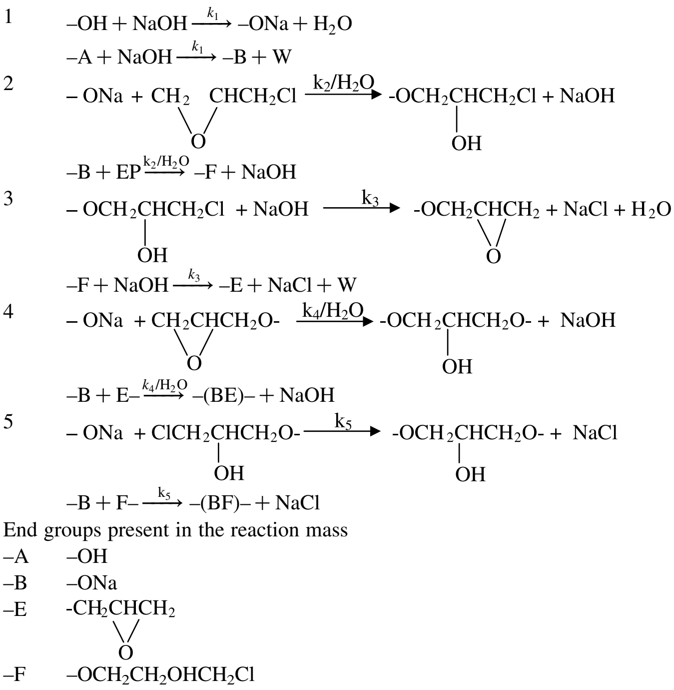
With all these studies, a perceived need is felt to organize an advanced analysis with all the valuable conclusions from earlier studies with many effective new optimization objectives. As the previous research works do not talk about the minimization of possible by-products, and minimization of the overall product stabilization time, etc., those objectives are added to the present work. Moreover, this study includes very close to experimental conditions for total addition of different reactants, the desired reactant's ratio (to minimize possible alkaline hydrolysis of epichlorohydrin) and maximization of desired lower chain polymers in a single framework. During this research activity, the basic stoichiometric proportionality has been kept very close to the available experimental conditions for which the model has been validated. This research study is expected to be close to actual realizations with a detailed analysis for most of the important aspects pertaining to the kinetic study for epoxy polymerization, which has not been done in any of the earlier research efforts in such an integrated framework.

Real-world optimization problems often demand to cater to the need of solving more than one objective, simultaneously. Multi-objective optimization problems (MOOP) lead to a set of optimal solutions, known as pareto optimal (PO) solutions, as opposed to the single solution provided by any single objective optimization task. Although only one solution must be chosen at the end of the optimization exercise and this often must be performed with the guidance of a decision-maker, it is a better practice to first find a set of PO solutions to have an idea of the extent of trade-offs possible among the underlying objectives before focusing on a particular solution [8]. Although the field of research and application on multi-objective optimization is not new, the use of evolutionary multiobjective optimization techniques in various engineering and business applications is a recent phenomenon. The desired objectives in a complex polymerization process often exhibit conflicting relationships and therefore become an ideal problem for multiobjective optimization studies. In this paper, multi-objective optimization of dynamic growth of selective species, during semi-batch epoxy polymerization is investigated. Similar successful applications can be found elsewhere [9–13]. This effort includes real-coded NSGA-II as an optimization tool, which seems to be much more powerful compared to popularly used binary-coded NSGA-II though these evolutionary methods are observed to be much more effective (as they generate a poorly spread PO solution set with much less computational effort for these kinds of complex nonlinear optimization problems) as compared to classical methods, i.e. the weight based method or ε-constrained method [16].

2. Model and problem formulation

The complete kinetic scheme for the above mentioned polymerization system is given in Table 1 [5]. Raha and Gupta [5] and Raha et al. [6] have validated the kinetic model with experimental data, provided by Batzer and Zahir [4] for oligomeric species, using the same scheme. Using the species balance approach, the ordinary differential equation-initial value problems (ODE-IVP) are derived for various species and their moments (Raha and Gupta [5]). These equations are solved by the Runge–Kutta (RK) [18] type explicit numerical integration routine and kinetic parameters appearing in the equations are estimated with the help of the genetic algorithm (GA).

Table 1
Reaction scheme for epoxy polymerization



1 $-OH + NaOH \xrightarrow{k_1} -ONa + H_2O$

$-A + NaOH \xrightarrow{k_1} -B + W$

2 $-ONa + \underset{O}{CH_2\ CHCH_2Cl} \xrightarrow{k_2/H_2O} -OCH_2\underset{OH}{CH}CH_2Cl + NaOH$

$-B + EP \xrightarrow{k_2/H_2O} -F + NaOH$

3 $-OCH_2\underset{OH}{CH}CH_2Cl + NaOH \xrightarrow{k_3} -OCH_2\underset{O}{CHCH_2} + NaCl + H_2O$

$-F + NaOH \xrightarrow{k_3} -E + NaCl + W$

4 $-ONa + \underset{O}{CH_2CH}CH_2O- \xrightarrow{k_4/H_2O} -OCH_2\underset{OH}{CH}CH_2O- + NaOH$

$-B + E- \xrightarrow{k_4/H_2O} -(BE)- + NaOH$

5 $-ONa + ClCH_2\underset{OH}{CH}CH_2O- \xrightarrow{k_5} -OCH_2\underset{OH}{CH}CH_2O- + NaCl$

$-B + F- \xrightarrow{k_5} -(BF)- + NaCl$

End groups present in the reaction mass

–A	–OH
–B	–ONa
–E	$-\underset{O}{CH_2CHCH_2}$
–F	$-OCH_2CH_2OHCH_2Cl$

The ‘state’ of the reaction scheme can be well described by a set of 48 state variables, ($\mathbf{x}=[x_1, x_2,\ldots, x_{48}]^T$), including all species balance and moment balance equations:

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

where **x** and **U** are vectors of the state and manipulated variables (intermediate addition amounts at different times), respectively. These equations can easily be written using species balance and equation of moments of various orders. The manipulated variable vector consists of three discrete addition profiles, namely, the profile for NaOH [$U_1(t)$], epichlorohydrin [$U_2(t)$] and bisphenol-A [$U_3(t)$]. The various molecular species including the monomer considered for the modeling exercise exist in the published article of Raha et al. [5]. The mole balance equations for the end groups and lower oligomers in the semibatch reactor, moment equations for various molecular species and the equations for number as well as weight average molecular weights have been utilized for this study. Given three discrete profiles (**U** at time zero and other time steps) and initial conditions of all state variables (**x** at time zero), the reaction scheme model can be integrated by the explicit RK type method until a polymer processing time (t_{sim}), to be defined externally, is reached. This simulation package is combined with real-coded non-dominated sorting genetic algorithm (NSGA II) optimization routine for performing multi-objective optimization [14–17].

Two different MOOPs are studied here. For both the cases, decision variables are **U** vector and t_{sim}. As t_{sim} is a decision variable, once a value of t_{sim} is selected by the optimization routine, each of these three ingredient profiles ($U_1(t)$, $U_2(t)$, $U_3(t)$) is discretized into seven equally spaced points (u_i) in between zero to t_{sim} hours (including both the end points) and additional amounts of ingredients at those addition points are decided. Each of these 21 decision variables is forced to lie between their lower (u_i^{min}) and upper (u_i^{max}) bounds. Another decision variable, t_{sim}, is also forced to lie between its lower (t_{sim}^{min}) and upper bounds (t_{sim}^{max}). Additional constraints are imposed on several other reaction performance parameters. The reasoning behind the selection of optimization objectives as well as constraints is discussed in the section below.

(1) Starting with the first optimization problem, the selection of limiting values of M_n and PDI (M_n^{min} and PDI^{max}) is based on the batch experimental data of Batzer and Zahir [4]. The quality of the polymer product ($M_n^{min} = 633.0$ and $PDI^{max} = 1.61$) generated out of that research work is taken as a minimum quality requirement for the present study. Moreover, those values are recorded at the seventh hour of the experimental period. But actually it has been seen (through simulation) that a lot of unstable species remain in the reaction mixture at the end of the seventh hour and that the product got a reasonably stabilized composition (more EE_n) only after 40 h with a PDI value more than 1.95. The present study tries to achieve a stable polymer product in much less processing time with a higher M_n and lower PDI specification. The overall objective is also to maximize EE_n (a spontaneous choice

out of this mechanistic description given in Table 1) in the final polymer product. Parallely, another need is to minimize the chain propagation with time, i.e. preferential production of lower oligomers as the subsequent major application of epoxy polymer is the curing process and that requires lower oligomers of the EE_n species.

(2) This polymerization process is generally contaminated with nine other polymer species other than EE_n. Some of them exist even in the stable product as impurities and the PDI became higher. So, an effort has been made to minimize their population in the final polymer latex. Minimization of their concentration is typically a time-dependent phenomenon and a lot of attention is required either to minimize or constrain the growth dynamics for those undesired but obvious polymer species.

(3) The major problems of computer simulations consist of their applicability in actual conditions. Normally every extrapolation from the model validation points is associated with gross errors. Here an attempt has been made to have the entire computational analysis very close to available experimental conditions within which the kinetic parameters are estimated. This attempt is supposed to reduce the extrapolation error. For that reason, constraints have been imposed on the system for different variables. For total additions of different reactants like NaOH, EP and AA_0, the amounts of additions are restricted and those restrictions are imposed based on the experimental conditions. Another important aspect is the ratio of EP and NaOH. Normally it has been seen as well as experienced by experimental works (Batzer and Zahir [4]) that concentration of EP/NaOH ratio is typically 3.0 or more at any point of time. The underlying reason is to avoid the probable alkaline hydrolysis of EP with more concentration of NaOH. To avoid that, current study also contains such constraints for the EP/NaOH ratio. In the second optimization problem, the AA_0/NaOH ratio is also taken very close to 1:1, as observed in the available experimental conditions. Though this ratio is not as critical as EP/NaOH ratio but stoichiometrically one molecule of AA_0 ideally requires one NaOH molecule to initiate the entire reaction process. Also, it is even more important to mention that without this restriction in the ratio of AA_0/NaOH, the AA_0 requirements are very few, as is evident in the results of the first optimization problem (given in Section 3). The amount of AA_0 critically limits the polymer production. Maintaining the 1:1 ratio thus helps in increase in the AA_0 requirement in this reactive system.

As mentioned earlier in this manuscript that this effort is greatly limited by the experimental data provided by Batzer and Zahir, the inclusion of EP hydrolysis in the reaction scheme is a difficult task to do due to lack of experimental information. However, as Batzer and Zahir did not experience any EP hydrolysis with a stoichiometric excess of EP over NaOH (3:1), we have strictly followed that ratio with an appreciation that most probably with that ratio, the chances of EP hydrolysis is remote. This is indeed a speculation but our intention is to be on the safer side of operation, especially when some of the quantification may become fuzzy due to lack of experimental evidence. It is also true that all three reactants require NaOH. But one thing is even more important that with the increase in NaOH additions, the probability of EP hydrolysis increases and with a 3:1 ratio (EP/NaOH), we are reducing that probability indirectly. From the mechanistic point of view, hydrolysis of EP normally happens with a concentrated solution of the base like NaOH, which is not so in our case.

(4) Unlike the first optimization problem, the second problem contains the objective of minimization of NaOH additions. This will help in extracting process benefits out of lower additions of reacting ingredients because minimum addition of NaOH also indirectly minimizes the additions of the other reacting species. Additionally, instead of minimizing the other species populations (excepting EE_n), those are treated as constraints and the upper limits of those constraints are taken from the information of the first optimization problem where those species are minimized. Here basic stoichiometry has been maintained with even more closeness with respect to the available experimental conditions.

So these optimization problems have 22 decision variables, 21 coming from discretized addition amounts (u_is) and one from the polymer processing time (t_{sim}).

$$
\text{Problem 1}\begin{cases}
\text{Maximize}\dfrac{\lambda_0^{EE}}{\lambda_0^{AA}+\lambda_0^{AB}+\lambda_0^{AE}+\lambda_0^{AF}+\lambda_0^{BB}+\lambda_0^{BE}+\lambda_0^{BF}++\lambda_0^{EF}+\lambda_0^{FF}}\\
\text{Minimize}\, t_{\text{sim}}\\
\text{Minimize}\dfrac{\lambda_1^{EE}}{\lambda_0^{EE}}\\
\text{PDI}\le \text{PDI}^{\max}\\
M_n \ge M_n^{\min}\\
\sum_{i=1}^{7} u_i \le 1.0\,(\text{for NaOH})\\
\sum_{i=8}^{14} u_i \le 3.0\,(\text{for EP})\\
\sum_{i=15}^{21} u_i \le 1.0\,(\text{for}\,AA_0)\\
\left(\dfrac{[\text{EP}]}{[\text{NaOH}]}\right)_t \ge 3.0\\
\text{mass and moment balance equations}\\
u_i(i=1,\ldots,21)\&t_{\text{sim}}\text{being decision variables}\\
u_1^{\min}=0.1;\ u_2^{\min}=u_3^{\min}=u_4^{\min}=u_5^{\min}=u_6^{\min}=u_7^{\min}=0.0\\
u_1^{\max}=u_2^{\max}=u_3^{\max}=u_4^{\max}=u_5^{\max}=u_6^{\max}=u_7^{\max}=1.0\\
u_8^{\min}=0.1;\ u_9^{\min}=u_{10}^{\min}=u_{11}^{\min}=u_{12}^{\min}=u_{13}^{\min}=u_{14}^{\min}=0.0\\
u_8^{\max}=u_9^{\max}=u_{10}^{\max}=u_{11}^{\max}=u_{12}^{\max}=u_{13}^{\max}=u_{14}^{\max}=2.0\\
u_{15}^{\min}=0.1;\ u_{16}^{\min}=u_{17}^{\min}=u_{18}^{\min}=u_{19}^{\min}=u_{20}^{\min}=u_{21}^{\min}=0.0\\
u_{15}^{\max}=u_{16}^{\max}=u_{17}^{\max}=u_{18}^{\max}=u_{19}^{\max}=u_{20}^{\max}=u_{21}^{\max}=1.0\\
t_{\text{sim}}^{\min}=0.0;\ t_{\text{sim}}^{\max}=7.0
\end{cases}
\qquad (2)
$$

$$\text{Problem 2}\begin{cases} \text{Minimize} \sum_{i=1}^{7} u_i \\ \text{Minimize}\, t_{\text{sim}} \\ \text{Minimize} \dfrac{\lambda_1^{EE}}{\lambda_0^{EE}} \\ \text{PDI} \le \text{PDI}^{\max} \\ \sum_{i=1}^{7} u_i \le 1.0 \\ \sum_{i=8}^{14} u_i \le 3.0 \\ \sum_{i=15}^{21} u_i \le 1.0 \\ \left(\dfrac{[\text{EP}]}{[\text{NaOH}]}\right)_t \ge 3.0 \\ \dfrac{\sum_{i=1}^{7} u_i}{\sum_{i=15}^{21} u_i} = 1.0 \left(\text{with} \pm 10\%\, \text{tolerance} - \text{for} \dfrac{\text{NaOH}}{AA_0}\right) \\ \left(\lambda_0^{AA} + \lambda_0^{AB} + \lambda_0^{AE} + \lambda_0^{AF} + \lambda_0^{BB} + \lambda_0^{BE} + \lambda_0^{BF} + \lambda_0^{EF} + \lambda_0^{FF}\right) \le 0.002 \\ \text{mass and moment balance equations} \\ u_i (i = 1,\ldots,21) \& t_{\text{sim}}\, \text{being decision variables} \\ u_1^{\min} = 0.1;\ u_2^{\min} = u_3^{\min} = u_4^{\min} = u_5^{\min} = u_6^{\min} = u_7^{\min} = 0.0 \\ u_1^{\max} = u_2^{\max} = u_3^{\max} = u_4^{\max} = u_5^{\max} = u_6^{\max} = u_7^{\max} = 1.0 \\ u_8^{\min} = 0.1;\ u_9^{\min} = u_{10}^{\min} = u_{11}^{\min} = u_{12}^{\min} = u_{13}^{\min} = u_{14}^{\min} = 0.0 \\ u_8^{\max} = u_9^{\max} = u_{10}^{\max} = u_{11}^{\max} = u_{12}^{\max} = u_{13}^{\max} = u_{14}^{\max} = 2.0 \\ u_{15}^{\min} = 0.1;\ u_{16}^{\min} = u_{17}^{\min} = u_{18}^{\min} = u_{19}^{\min} = u_{20}^{\min} = u_{21}^{\min} = 0.0 \\ u_{15}^{\max} = u_{16}^{\max} = u_{17}^{\max} = u_{18}^{\max} = u_{19}^{\max} = u_{20}^{\max} = u_{21}^{\max} = 1.0 \\ t_{\text{sim}}^{\min} = 0.0;\ t_{\text{sim}}^{\max} = 75.0 \end{cases} \tag{3}$$

NSGA II is used to solve these multi-objective optimization problems. Each solution is represented as a real-valued vector of 22 values indicating the addition of NaOH, EP, AA_0 at different time steps and a value of polymer processing time, t_{sim}. For the real coded NSGA-II, we use the simulated binary crossover (SBX) and the polynomial mutation operators [16]. When a pre-specified maximum iteration count ($N_{\max}$) is reached, NSGA-II is terminated and the non-dominated solutions of the final population are declared as the obtained PO solutions. For both the cases, $N_{\max}=300$ and a population size of $N_{\text{pop}}=250$ are used. The crossover and mutation probabilities of $p_c=0.9$ and $p_m=0.1$ are used.

3. Results and discussions

Model tuning with available experimental data has been given in the Appendix A. It is realized from earlier studies that irrespective of batch or semi-batch operations, various species specially with the B end group (BB_n, BE_n, BF_n, etc.) deplete during prolonged hours of processing and ultimately convert to EE_n, EF_n and FF_n. Generally, EE_n dominates in the final product both in its concentration and chain length. Probably the stoichiometric excess of epichlorohydrin taken initially ensures ultimate transformation to maximum EE_n species at prolonged processing time. The prolonged operation as mentioned here is of the order of 43 h in case the polymerization occurs in the batch mode for the data of Batzer and Zahir [4] (simulated performance of the available experimental conditions in Fig. 1). So through this optimization study, the aim is to grow EE_n as much as possible without spending that much time with the process conditions close to available experimental conditions. This is indeed a hard task as the populations of polymeric species with B ends (unstable species) are usually high as time grows, especially in the initial processing period. The growth curves for AA_n, AB_n, BB_n are absent in Fig. 1, as their initial population is high enough to mask the other distributions, but after 20 h of processing time, they become insignificant.

An effort was made to restrict the additions (to make them close to the available experimental conditions) in the defined optimization problems (Problems 1 and 2). Epichlorohydrin is maintained at least at a three-times higher level than NaOH throughout the reaction process to prevent its alkaline hydrolysis. The achieved benefit out of the optimization problems is grossly defined by a parameter called 'space-time productivity'. The space-time productivity with respect to the simulated result of the experimental data of Batzer and Zahir [4] is defied here as:

(Time required for EE_n maximization for the case of Batzer and Zahir [4]/time required for EE_n maximization for the present case)×(concentration of AA_0 for the present case/concentration of AA_0 for the case of Batzer and Zahir [4]).

The typical value of space-time productivity became (43 h/5.9 h)×(0.14 kmol/m^3/0.4 kmol/m^3) = 2.55 for a case

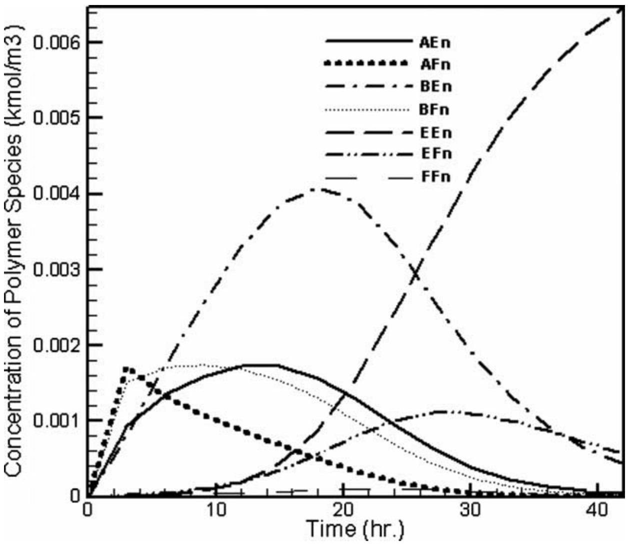


Fig. 1. Species distribution for the batch process data of Batzer and Zahir [4] (NaOH = 0.4 kmol/m^3, EP = 1.28 kmol/m^3 and AA_0 = 0.4 kmol/m^3).

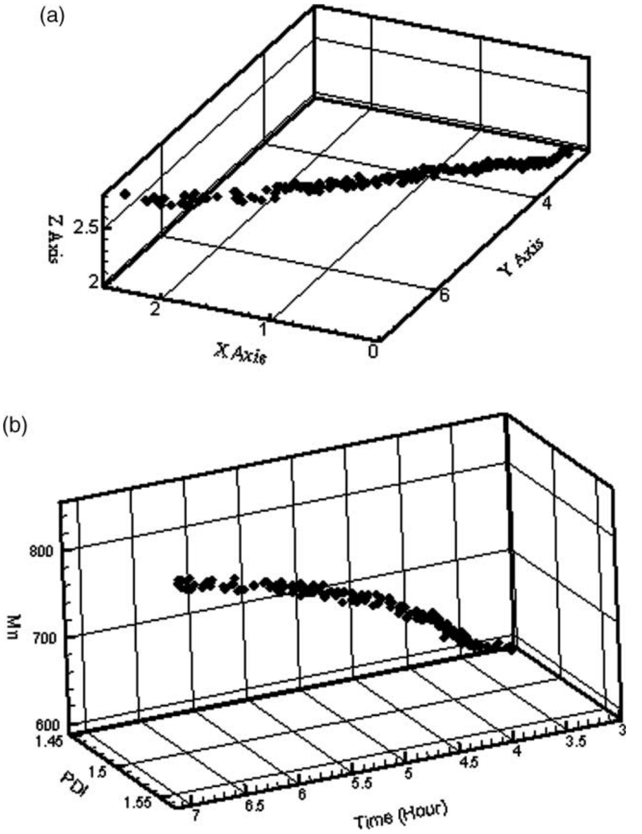
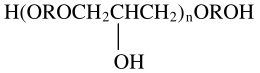
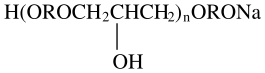
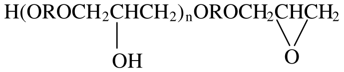
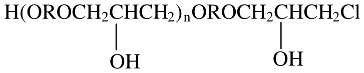
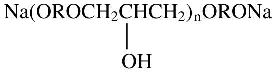
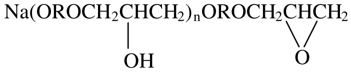
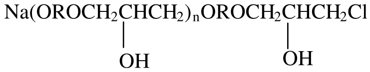
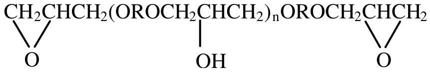
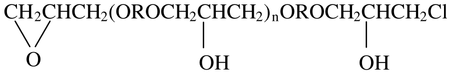
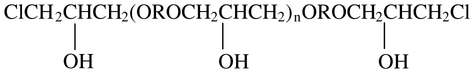
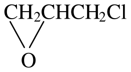
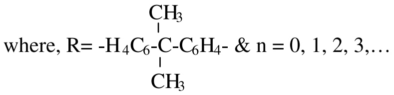


Fig. 2. (a) Multi-objective Pareto set description for the 1st optimization problem (X-axis: objective 1 of problem 1, Y-axis: objective 2 of problem 1, Z-axis: objective 3 of problem 1); (b) optimized M_n and PDI patterns with time for the same optimized points given in (a).

Table 2
Different molecular (monomer and polymer) species present in the reaction mass

AA_n	 $\mathrm{H(OROCH_2\underset{OH}{CH}CH_2)_nOROH}$
AB_n	 $\mathrm{H(OROCH_2\underset{OH}{CH}CH_2)_nORONa}$
AE_n	 $\mathrm{H(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{\diagdown O \diagup}{CHCH_2}}$
AF_n	 $\mathrm{H(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{OH}{CH}CH_2Cl}$
BB_n	 $\mathrm{Na(OROCH_2\underset{OH}{CH}CH_2)_nORONa}$
BE_n	 $\mathrm{Na(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{\diagdown O \diagup}{CHCH_2}}$
BF_n	 $\mathrm{Na(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{OH}{CH}CH_2Cl}$
EE_n	 $\mathrm{\underset{\diagdown O \diagup}{CH_2CH}CH_2(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{\diagdown O \diagup}{CHCH_2}}$
EF_n	 $\mathrm{\underset{\diagdown O \diagup}{CH_2CH}CH_2(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{OH}{CH}CH_2Cl}$
FF_n	 $\mathrm{ClCH_2\underset{OH}{CH}CH_2(OROCH_2\underset{OH}{CH}CH_2)_nOROCH_2\underset{OH}{CH}CH_2Cl}$
EP	 $\mathrm{\underset{\diagdown O \diagup}{CH_2CH}CH_2Cl}$


where, $\mathrm{R= -H_4C_6\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}C_6H_4\text{-}}$ & n = 0, 1, 2, 3,…

among the optimized solutions (for problem 1) in Fig. 2. Among many optimal solutions, the value of space-time productivity can be as high as 3.0 for the first optimization problem. Actually, with a stoichiometric excess of EP and NaOH, AA_0 determines the polymer production. That is why, for the calculation of space-time productivity, the concentration of AA_0 is used. PDI is much less even in that short processing time and its value is 1.54 for the case given in Fig. 2. So, one can expect higher productivity with a much better quality for the desired polymer product. Fig. 2(a) shows the multi-objective Pareto for all 3 optimization objectives for problem 1. Fig. 2(b) represents the variations of M_n and PDI with the time objective for the same optimized points in Fig. 2(a). As expected, both M_n and PDI values increase with polymer processing time. For the cases with higher M_n with higher EE_n concentration, some other species grow slowly (mostly FF_n, EF_n in Table 2) for which PDI is more for those and the time requirement for these types of processes are also on the higher side. All points in Fig. 2 are the optimized set and real coded NSGA-II ensures that those are supposed to be the best available operating points based on the definition of the first optimization problem. It is now the engineering judgments of the users that are required to choose a suitable operating condition for the operating objectives. For example, if somebody is more interested in the quality of a polymer, he/she can go down in the PDI (in Fig. 2(b)) axis and fix other objectives, subsequently. Actually, for an optimized Pareto set, an improvement in one objective can definitely be associated at the cost of other objectives. Every case in Fig. 2 is associated with a typical optimized addition strategy and interestingly, those addition strategies for Fig. 2 follow some patterns (Fig. 3(a)–(c)), which can help the researchers to extract the underlying theoretical basis for them. Though the ingredient addition amounts at various time steps are discrete, they are joined with straight lines to extract the trends. With an equal interval addition strategy, additions can be at any time depending upon the total processing time. So, the x-axis is the number of additions (a fixed number, i.e. seven here) not the time of additions. From different patterns of Fig. 3, one can say that AA_0 is very critical to initiate the reaction process with NaOH (Table 1) and then epichlorohydrin and NaOH are engaged in forming intermediate unstable species, which suffer further depletion to produce desired polymer species. Epichlorohydrin shows high values of additions since, to order to maximize EE_n, one has to ensure the substantial presence of epoxy groups that are present in both the sides of EE_n species. Bisphenol-A is required initially to start the polymerization process, but later on, its requirements are present only in chain growing steps (steps 4 and 5 in Table 1) and all these steps explain the obtained trends. These kinds of rules or trends coming out of the analysis of this MOOP

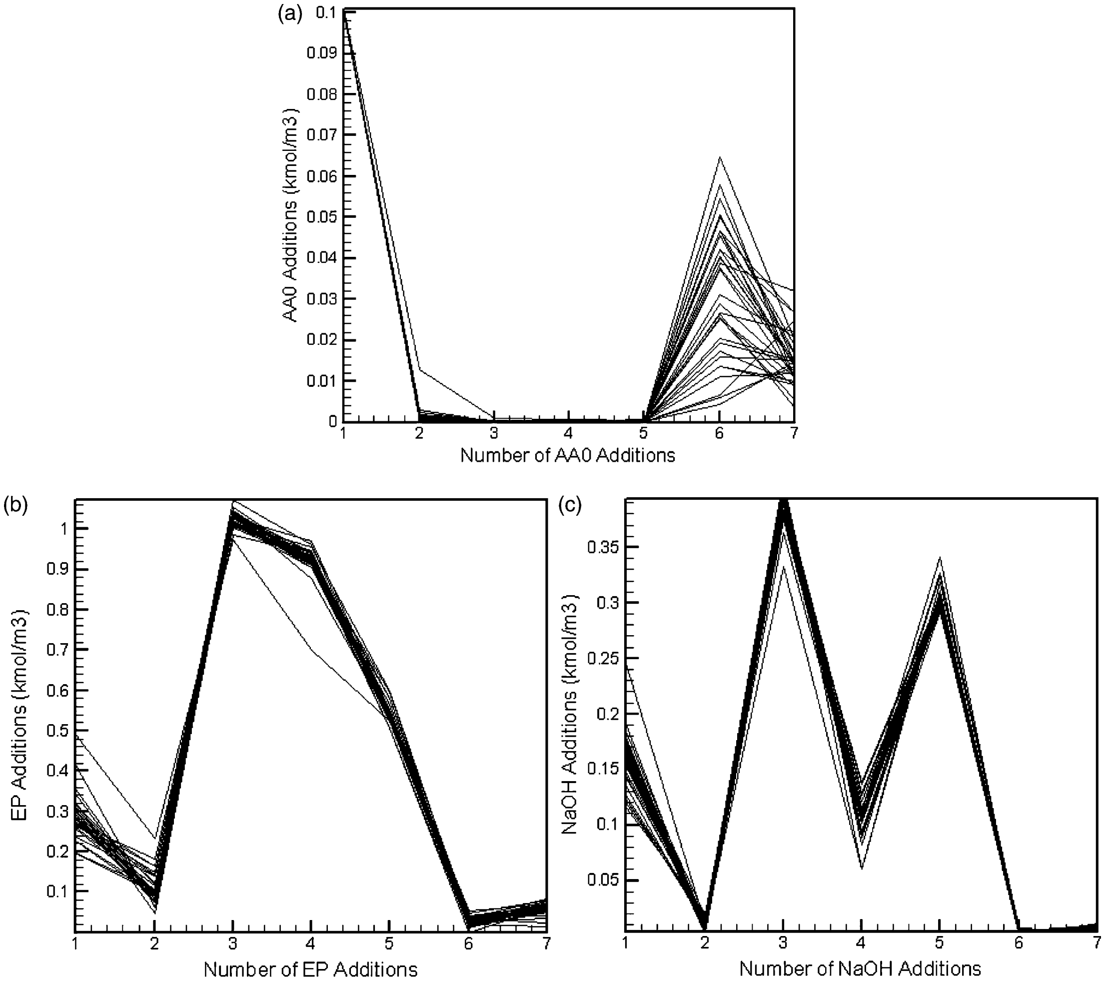


Fig. 3. (a) Optimized addition patterns for AA_0 (b) optimized addition patterns for EP and (c) optimized addition patterns for NaOH respectively (for first optimization problem).

exercise can be of tremendous use as far as the operators are concerned.

Current definition of the first optimization problem produces much larger operating choices, for example M_n varies from 600 to 800 with a PDI variation of 1.46–1.61. So, AA_0 additions have occurred in different quantities for different optimized cases, and those are causing the wide variation in the values of optimization objectives or in other variables like M_n and PDI. Variations in the amount of EP and NaOH are fewer and they have very distinct patterns. All of the reactants have very critical requirements in the beginning, as initial reactions require all three reactants together (Table 1). EP is a building block for the desired polymer species, so its requirement became higher in the later half of the reaction process, where chain growth is important. NaOH is required to a higher extent as NaOH helps in producing unstable species and a good population of those unstable species depletes further to give a desired polymer growth. Fig. 4 shows the species distribution for one of the optimized points in the PO set of solutions for the first optimization problem. Compared to Fig. 1, improvements are clear in terms of EE_n maximization and reduction in processing time with higher space-time productivity (for problem 1).

Here the chain length (as evident in Fig. 2(a)) is restricted quite effectively with a relatively lower processing time. Few things are still left to be achieved from this optimization study. Those are (a) undesired species are present, though much fewer, when compared to the seventh hour species distribution in Fig. 1; (b) instead of oligomers, lower chain polymers are generated; (c) additions of NaOH is on the higher side of the given bound (Eq. (2)). The species like FF_n, EF_n are also unstable species and the end solution may have a chance to deplete further, which is not desirable. Actually, the other species concentrations are in the denominator of the objective 1 in Eq. (2) and while maximizing the objective 1, this denominator is supposed to be minimized automatically. But ultimately, this maximization of objective 1 with the simultaneous minimization of objective 2 (time) and 3 (chain length) suffers a strong trade-off with each other and thus the minimization of other species within short processing hours (7 h) was not obtained satisfactorily. But this optimization gives a good idea about the species distribution and their respective value during the operation, which has been used in the second problem to define a constraint for other undesired species' concentrations. Also, an attempt is required to further reduce the additions of reactants.

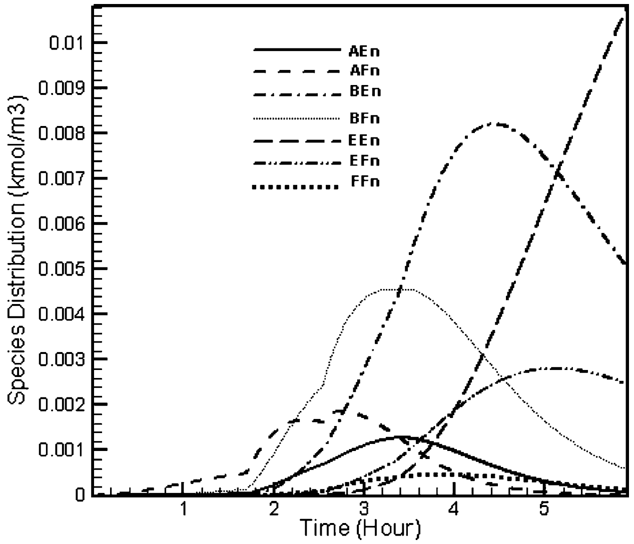


Fig. 4. Species distribution for one optimized point in the PO set of solutions for the first optimization problem (total NaOH = 0.9 kmol/m^3, total EP = 2.9 kmol/m^3 and total AA_0 = 0.14 kmol/m^3).

Though the first optimization problem clearly shows the process benefit out of it, the varied nature of the optimum performances (huge variations in M_n and PDI) allows a variety of different operating strategies. Additionally, though the minimization of the probable alkaline hydrolysis of EP has been achieved quite successfully in the previous problem, proportionality between NaOH and AA_0 is not present. Actually, lower concentration of AA_0 critically limits the polymerization process. Also, the available experimental data by Batzer and Zahir [4] shows a typical proportion among all three ingredients (AA_0:NaOH:EP = 1:1:3). Deviation from that proportionality means a probable departure from the validated operational zone. Here, due to the minimization objective for NaOH, additions are further reduced and become even closer to available experimental conditions. Typical average space-time productivity can be as high as 5.0 for some of the optimized cases in problem 2. Fig. 5(a) and (b) show the optimization plots for this present case (problem 2). Here, two additional important features are the lower amount of addition and tighter operating choices. So, one can achieve a very good process performance with minimum additions. Obviously, this case has suffered with respect to process performances compared to Fig. 2. More processing time is required here with relatively higher PDI. Reasons for this are the imposed constraints on basic stoichiometry and the huge decrease of undesired by-products, which are additionally imposed on the second optimization problem formulation. Here, the addition patterns are shown in the Fig. 6(a)–(c). Trends are little different from the trends of the first optimization problem. Initial NaOH additions are less due to the fact that the minimization of NaOH addition is treated as an optimization objective. The addition of AA_0 is more in the later half of the process to gain the proportionality with NaOH (as the 1:1 ratio has to be maintained to remain in the vicinity of available experimental conditions) and the amount of AA_0 is more compared to the case of problem 1 (as the requirement of NaOH is fairly high in most of the reaction steps). More AA_0 and lower processing time (with respect to the case of Batzer and Zahir [4]) are the reasons behind the higher increase in space-time productivity compared to the case of problem 1. EP additions also came down much earlier compared to those in Fig. 3(b) (problem 1). The probable reasons may be the minimization of NaOH and proportionality of NaOH with AA_0. With a relatively lower amount of these two reactants, attaining lower chain length would have been a difficult task if EP is added to the system in higher amounts in the later half of the process, where mainly the chain growth progresses. Fig. 7 shows the corresponding species distribution for one of the optimum data from Fig. 5. One can see the clear differences for most of the species compared to Figs. 1 and 4. It shows a nicely controlled growth for the species EE_0, whereas all other species are minimized throughout the entire processing time. This clearly indicates the benefits of this present study compared to the case of Batzer and Zahir [4]. Also, this optimization problem is allowed to go for a slightly higher processing time compared to the case in problem 1.

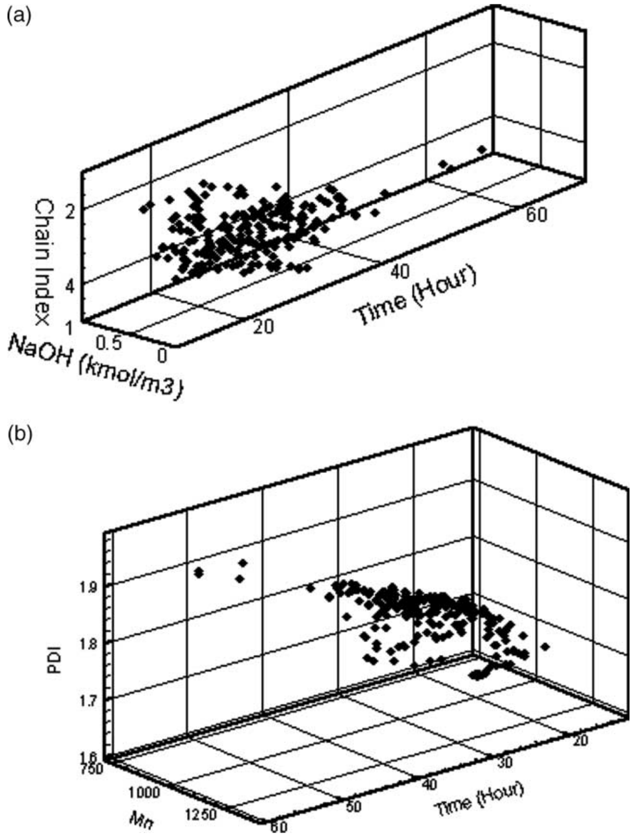


Fig. 5. (a) Multi-objective Pareto set description for the second optimization problem (*X*-axis: objective 1 of problem 2, *Y*-axis: objective 2 of problem 2, *Z*-axis: objective 3 of problem 2); (b) optimized M_n and PDI patterns with time for the same optimized points given in (a).

Here, one of the main objectives is to see the effect of discrete additions for more processing time over the optimized performance of epoxy polymerization to minimize the possible by-products. For the first problem, minimization of the quantity of by-products happens to the extent of 0.007 kmol/m^3

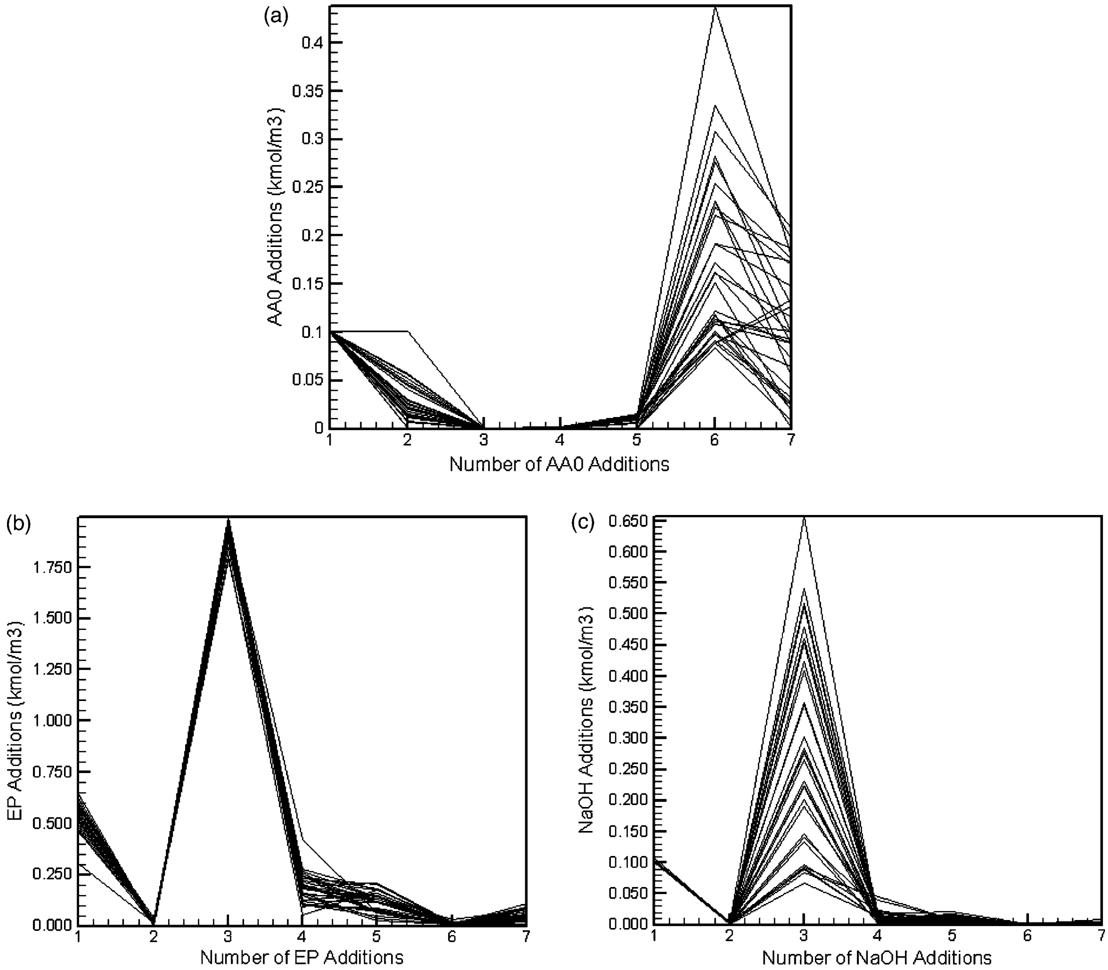


Fig. 6. (a) Optimized addition patterns for AA_0 (b) optimized addition patterns for EP and (c) optimized addition patterns for NaOH, respectively (for second optimization problem).

(summation of all by-products), whereas for the second problem, the summation came down to 0.002 $kmol/m^3$. Actually, in the first problem, this minimization was a part of the first objective (denominator), and in presence of multi-objective trade-off with processing time, the minimization suffered. The reason is very straight-forward as with more processing time, the quantity of byproducts reduces. In the first case, it was not allowed to have processing time more than 7.0 h, while in the second case, that allowance was upto 75 h. The whole intention was to provide different solutions for different users. For a lower processing time, the first problem and its solutions may be the probable answer, whereas for better product quality, space-time productivity and stability, one should look for the second optimization problem. Fig. 8 shows how the important variables like PDI, M_n, and EE_0 vary with three different objectives in problem 2 (Eq. (3)). One can find a strong trade-off between variables, such as if someone wants more desired species' concentration with lower chain length, he/she has to be ready for relatively more PDI. Here, one can see that having higher M_n, higher EE_0 and lower PDI is almost an impossible task due the strong multi-objective trade-off. Still, one can attain higher EE_0 concentration, lower PDI, lower processing time and lower chain length, but at the cost of

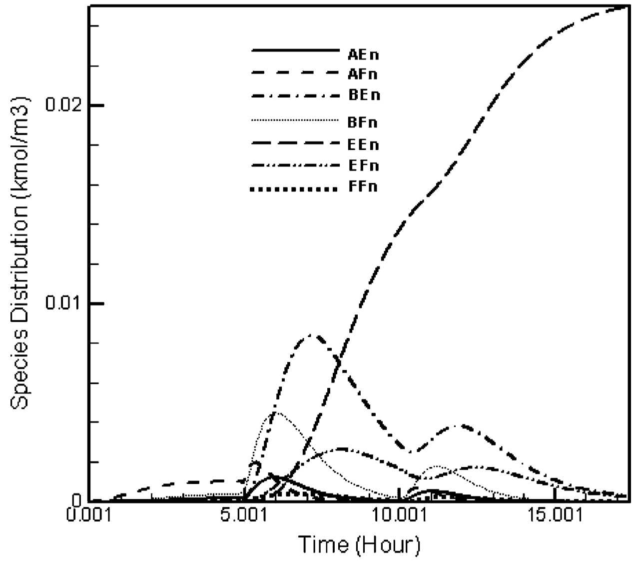


Fig. 7. Species distribution for 2nd optimization problem (total NaOH = 0.8 $kmol/m^3$, total EP = 2.8 $kmol/m^3$ and total AA_0 = 0.8 $kmol/m^3$).

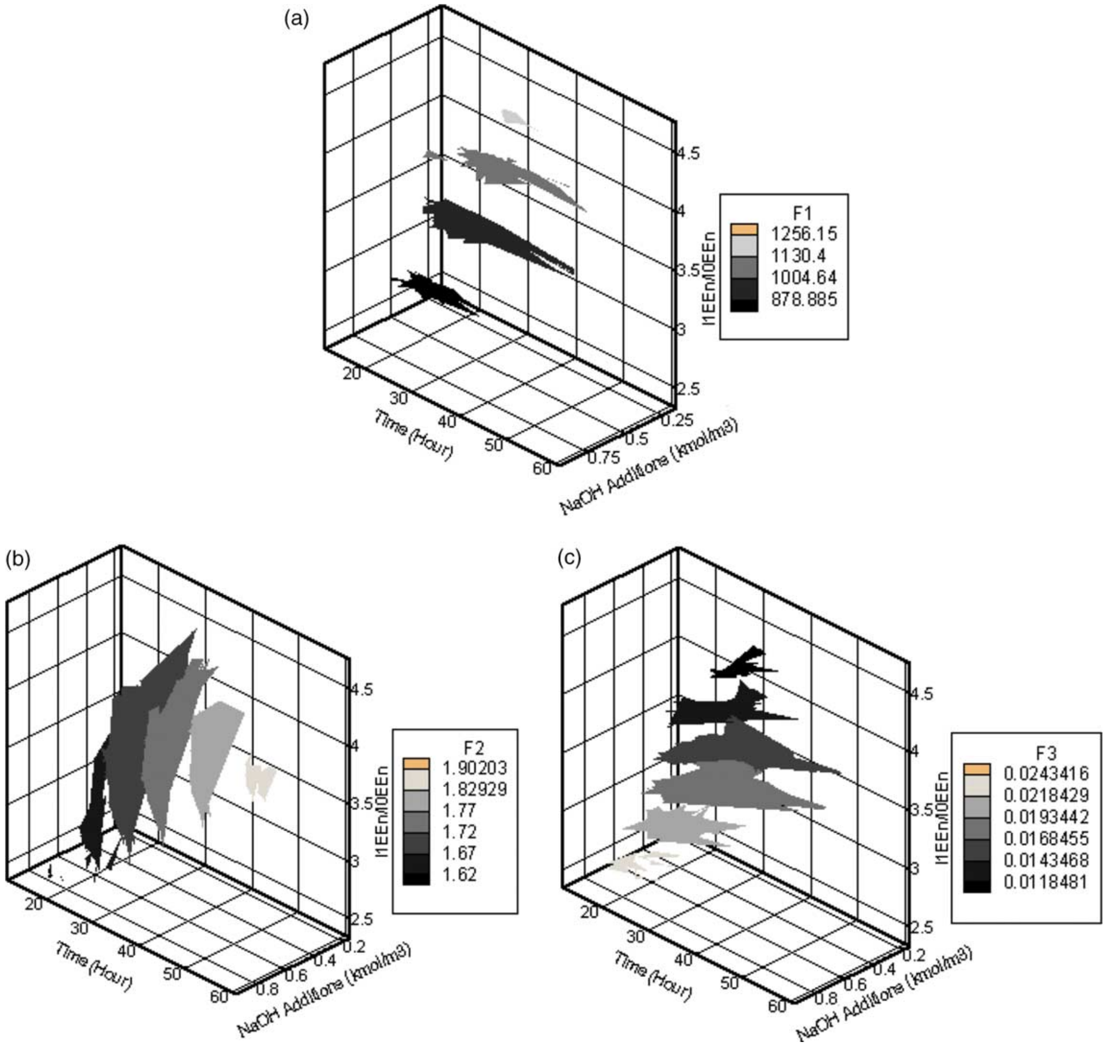


Fig. 8. Optimized contour of different variables (F1, M_n; F2, PDI; F3, Conc. of EE_0) with respect to three optimization objectives in problem 2.

lower M_n and higher additions. Nonetheless, all those data are optimized data, so one may travel towards different destinations of all these optimized plots depending on his/her process objectives. Closeness to the available experimental conditions in terms of the quantity of additions, proportionality among the different reactants targets the application of these simulation results towards practical uses. Problem 1 gives a rosier picture with respect to process performance (excellent reduction in processing time), whereas problem 2 sticks to the basic stoichiometry as observed in the available experimental conditions with a fair improvement for the process performances.

Though both the optimization problems with different optimization objectives show reasonable process improvements, and at the same time, basic similarity between their results, proves their individual robustness. The authors felt that the second problem may have all the required features and thus can be regarded as the more robust, practical and efficient optimization strategy between the two. Here, space-time productivity is more, additions are reduced, basic stoichiometry has been maintained and most importantly, the by-product reduction is remarkably good. Both the optimization exercises are built near to available experimental conditions, so that the results can be relied upon. Different measures like the EP-NaOH ratio (minimization of the alkaline hydrolysis of EP), restrictions of chain growth (selective increase for lower chain polymers), etc. impose realities over the simulations. Another thing was also clear from these two optimization problems, that even if someone requires to produce preferential oligomers, he/she will end up with small polymers (chain length little higher than 2.0). If at all, small oligomers are produced in this given framework, the polymer solution will have good quantities of other undesired polymer species, which is very damaging for both the quality as well as the stability of the final polymer latex. This is because of the fact that the minimization of by-products, lower chain length, and greater EE_n concentration, etc. are highly conflicting to each other and attainment of lower chain length (specifically for oligomers) means lower processing time as the growth of the chain length is purely a time dependent phenomenon. Obviously, in that early stage, the polymer solution will be contaminated with most of the undesired by-products (and thus be an unstable and lower purity product) with lower concentration of EE_n, as well.

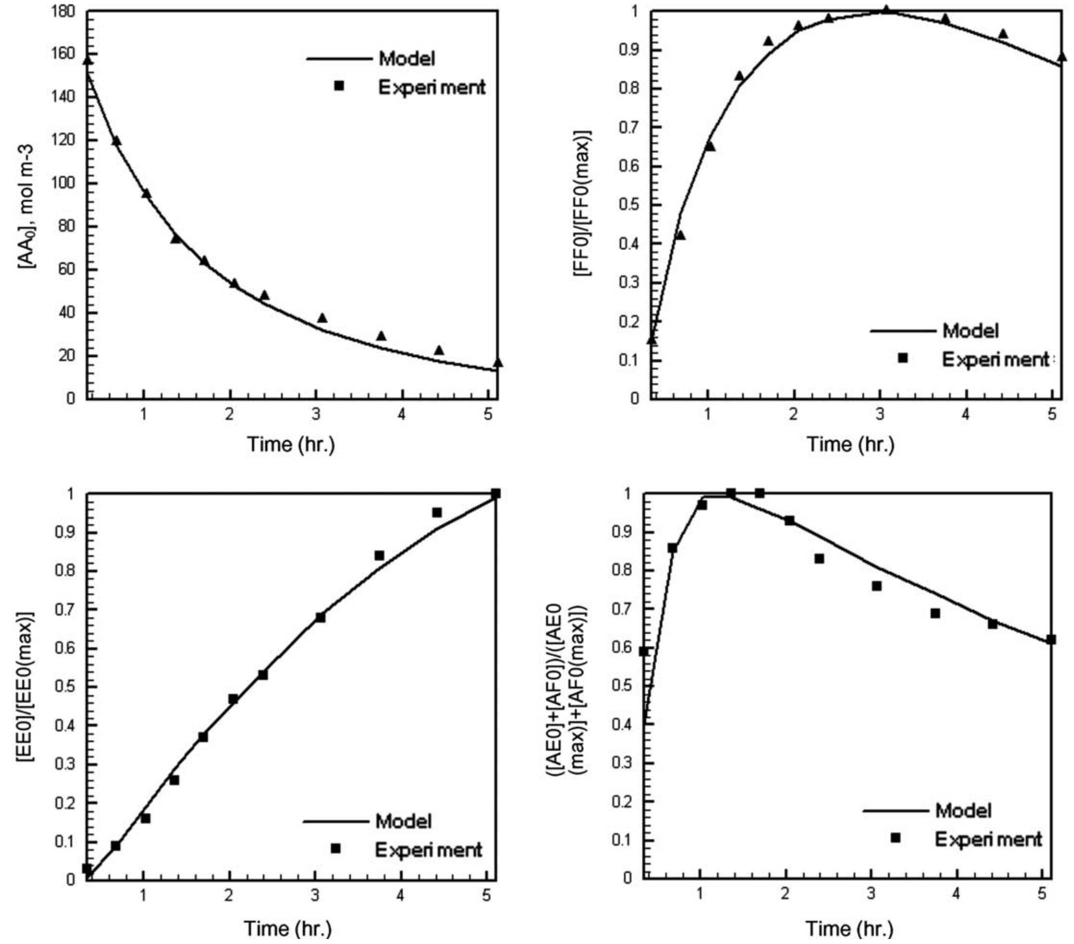


Fig. A1. Comparison of experimental data for some oligomers and model prediction using kinetic parameters evaluated by the Simple genetic algorithm.

With this present effort, real-coded NSGA-II shows tremendous potential to be applied in non-linear modeling aspects of process engineering applications. Each one of the two problems, when tested with any of the classical optimization methods (weight-based approach, ε-constraint approach), leads to poor distribution of PO points in the final Pareto set. The biggest advantage of NSGA II is its delivery of better PO solutions in a single simulation run, which is not possible with any of the most popularly used two classical optimization techniques mentioned above.

4. Conclusion

A species balance approach is used for moment-based modeling of a semi-batch epoxy polymerization process with two advanced optimization strategies, which are performed to come up with such process conditions for which the selective growth of a particular polymer species is maximized in the minimum possible processing time. Multi-objective optimization of three conflicting objectives is solved using real-coded NSGA II, and Pareto optimal solutions are obtained. Minimization of the chain length for subsequent applications of the epoxy polymer has also been treated as an optimization objective. Growth of other species (other than EE_0) is also minimized. Additions are reduced; basic stoichiometric proportionality has been maintained with an effective increase of spacetime productivity. The decision variables are the polymer processing time and discrete addition rate of various ingredients at different time steps, whereas satisfactions of all species balance equations, bounds on decision variables and some lower bounds on M_n as well as the upper bound on the PDI are treated as some of the constraints. Some realities like probable alkaline hydrolysis of EP is also taken care of in this analysis. Important conclusions are as follows:

(a) The mechanistic description of reactions in Table 1 spontaneously results in a selective growth of the EE_n species;
(b) Except for EE_n, all other species contribute insignificantly in the final product composition for optimized operations;
(c) If catalytic activity of NaOH is maintained properly, substantial reduction in processing time and PDI are possible;
(d) Keeping EP on the higher side, the NaOH with AA_0 determines the actual dynamics of the epoxy process;
(e) Space-time productivity, as well as quality (in terms of PDI and M_n) can be increased significantly with the selective growth of the desired species;
(f) Optimization with more processing time with longer additions can lead to a better control over the process;

(g) For a stable, good quality epoxy polymer product, preferential oligomer productions for the desired species are ruled out. At the same time, very small polymers (for the desired species) can be produced with high quality, good stability and in fairly less processing time;
(h) Population-based evolutionary algorithm for multi-objective optimization (like NSGA-II) performs extremely well with robustness not only in determining concave Pareto fronts but also in terms of PO point density on the same front.

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Appendix A

Experimental data on isothermal (25 °C) polymerization of bisphenol-A with epichlorohydrin have been provided by Batzer and Zahir [4]. The only data available was the data for some lower oligomeric species, which was used for model tuning. Using these experimental data, the optimal values for the rate constants are estimated. For this parameter tuning exercise, a simple genetic algorithm (SGA) is used. The objective here is to minimize an objective function that is chosen as a weighted sum of absolute errors between the values predicted by the model and experimental data. This is given by:

$$E(k_1,k_2,k_3,k_4,k_5) = \sum_j W_j \frac{1}{N_{j,\mathrm{exp}}} \sum_i \left[\frac{[j]_{i,\mathrm{theor}} - [j]_{i,\mathrm{exp}}}{[j]_{i,\mathrm{exp}}}\right]^2 \tag{A1}$$

where, E, W_j, $N_{j,\mathrm{exp}}$, k_1, k_2, k_3, k_4, k_5, $[j]_{i,\mathrm{theor}}$, $[j]_{i,\mathrm{exp}}$ are error function, jth weight for jth type experimental data, number of data points in jth type of experimental data, kinetic constant for jth reaction of Table 1 ($j=1,2,\ldots,5$), model prediction for ith data point in jth type of experiment and ith experimental data point in jth type of experimental data, respectively.

The problem addressed above can be expressed in the standard non-linear programming (NLP) problem as follows:

$$\begin{array}{lll} \text{Objective Function} & & \text{Min E} \\ i\text{th decision Variable}: & k_i^L \le k_i \le k_i^U & \text{for } i = 1,2,\ldots 5 \end{array} \tag{A2}$$

Superscript L and U denote the lower and upper bounds of the decision variables. The best-fit values of the rate constants are used to generate concentration profiles of several low molecular weight oligomers (Table 2). Fig. A1 demonstrates the model fit with some of the experimental data.

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