Kinetic Analysis and Multi Objective Optimization of L-Lactide Polymerization

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Abstract - Biopolymers have emerged as an appropriate replacement for conventional petrochemical polymers consoling our environmental concern. As an alternative to polyolefin, polylactic acid (PLA) has been identified as a capable biodegradable polymer. Lactide ring opening polymerization (ROP) has been demonstrated to be an efficient polymerization method. A well validated moment based kinetic model for lactide ROP referring with homogeneously well stirred batch reactor using 2-ethylhexanoic acid tin (II) salt as the catalyst and an alcohol as co-catalyst has been utilized to formulate the multi objective optimization problem (MOOP). The MOOP is composed of three conflicting objective functions: minimization of time, minimization of PDI and maximization of number average molecular weight (Mn). Decision variables have been implemented to analyse the process performance with the mass balance equation for objective function ranges as constraints. The optimization problem does not contain a single solution but rather contains several equally important solutions (Pareto front) which are called as non-dominated solutions and this Pareto front is obtained by using non-dominated sorting genetic algorithm-II (NSGA II) developed by Deb, 2001. Some of the Pareto front points showed better outcomes rather than the experimental data. The distinct aspect of modeling and optimization from experimental data can be applied directly in the actual large-scale plants.

Keywords: Poly(Lactic acid), Ring Opening Polymerization, Multi-objective optimization, NSGA-II.

1. Introduction

Biopolymers' eco-friendliness and biodegradability have opened a new chapter in environmental stability by replacing petroleum products. The remarkable physical properties of Poly (lactic acid) (PLA) made it an obvious choice for replacing polyolefins. They are ideal for biomedical applications such as tissue engineering, advanced pharmaceuticals, drug delivery, as well as in food packaging [1]. Among several polymerization methods, ring opening polymerization (ROP) of lactide has become most popular due to its better reaction control in producing high molecular weight PLA and increased productivity. As long as the unreacted monomer is present in the system, lactide ROP exhibits living behaviour. Catalysts have a unique position in the polymerization process. Among the various catalysts, FDA-approved Sn(oct)$_2$ is widely used. Although, researchers have recently successfully developed various complexes of zinc and iron for lactide polymerization [2].

The reaction mechanism for lactide polymerization has been investigated by various researchers. Penzcek et al [3] proposed a comprehensive kinetic scheme that included the polymer end chain inter-change reaction known as transesterification as well as chain transfer. The trans-esterification reaction is active along a reversible propagation path, and it is responsible for the wide molecular weight distribution (MWD). The overall reaction mechanism for l-lactide ROP is reversible chain reactions such as initiator activation, chain initiation (alkoxide initiation mechanism), propagation, chain transfer, inter and intra trans-esterification, and non-radical random chain scission [4]. In general, industrial PLA production is carried out at higher temperatures in order to achieve a faster reaction rate. Under these conditions, polymer chain degradation is unavoidable, especially at temperatures above 180°C. Optimizing the polymerization process at a lesser temperature is inevitable.

Multi objective optimization techniques determine the optimal solutions that are inherently conflicting, such as achieving maximum molecular weight and minimum polydispersity index in less polymerization time in a polymerization setup. Tsoukas et al. [5] and Fan et al. [6] were among the first to attempt to solve multi objective optimization problems (MOOPs) in polymer reaction engineering. In MOOP, a vector approach in which all objectives are considered simultaneously. This evolutionary approach can generate a large number of well-spread Pareto optimal (PO) solutions in a single optimization run. Mitra et al. [7] and Majumdar et al. [8] conducted detailed multi objective optimal control studies with relevant process

constraints to determine optimal addition profiles for the reagents that would further support semi-batch operation than conventional batch process.
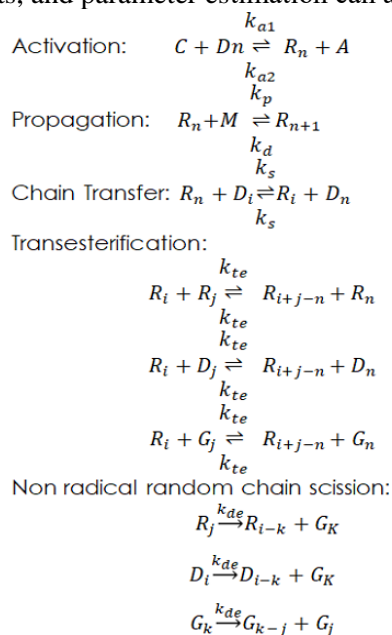
In this study, we proposed a multi objective optimization problem using a well-validated kinetic model with relevant constraints and decision variables operated at 180°C. L-lactide reaction mechanism is investigated with a wide range of monomer/initiator and co-initiator/initiator ratios, demonstrating that the initiator and co-initiator affect reaction rate and molecular weight. 2-ethyl hexanoic acid tin (II) salt as the catalyst and 1-dodecanol as a co-catalyst are considered in l-lactide ROP. NSGA II developed by Deb [9] is used to solve conflicting objective functions such as maximising the number average molecular weight (Mn) while minimising the polydispersity index (PDI) and time. The obtained pareto front solutions allow the decision maker to select the appropriate reagent profiles without fail.

2. Formulation and optimization aspects
2.1. Model

The entire Reaction scheme for the linear lactide ROP reaction mechanism is given in figure 1. Yu et al [4]. developed the kinetic scheme to model a batch polymerization process and validated the model results using experimental data. The process modelling includes the formulation of mass and population balance equations for twelve distinct species. These equations give a system of ordinary differential equations initial value problems (ODEIVP), which is solved using an explicit RK type technique that has been analysed. Some of the kinetic parameters (ka1, ka2, kp, kd, ks,) are estimated from experimental data using the Arrhenius equation. The rest of the kinetic parameters (kte, kde) are estimated by fitting the model. Monomer, catalyst, and co-catalyst concentrations were taken as the variables.

ODEs are derived from the kinetic model, and moment methods are used to simplify the reaction mechanism for use in MATLAB. The ring opening polymerization process, all molecular species used in the modelling, simulation details, all derived ODEs and corresponding results, and parameter estimation can all be found in Yu et al's work.

Activation: $C + Dn \underset{k_{a2}}{\overset{k_{a1}}{\rightleftharpoons}} R_n + A$

Propagation: $R_n + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} R_{n+1}$

Chain Transfer: $R_n + D_i \underset{k_s}{\overset{k_s}{\rightleftharpoons}} R_i + D_n$

Transesterification:

$R_i + R_j \underset{k_{te}}{\overset{k_{te}}{\rightleftharpoons}} R_{i+j-n} + R_n$

$R_i + D_j \underset{k_{te}}{\overset{k_{te}}{\rightleftharpoons}} R_{i+j-n} + D_n$

$R_i + G_j \underset{k_{te}}{\overset{k_{te}}{\rightleftharpoons}} R_{i+j-n} + G_n$

Non radical random chain scission:

$R_j \overset{k_{de}}{\rightarrow} R_{i-k} + G_K$

$D_i \overset{k_{de}}{\rightarrow} D_{i-k} + G_K$

$G_k \overset{k_{de}}{\rightarrow} G_{k-j} + G_j$

C: catalyst(Sn(oct)$_2$), A: octanoic acid, M: Monomer, R_n: active chain (propagating chain), D_n:

Dormant chain (reversibly terminated chain), G_n: Dead chain (irreversibly terminated chain),

n, j, k, i: corresponding length of the chains.

Figure 1. Reaction scheme for ring opening polymerization of lactide

2.2. Multi Objective Optimization

Objective function is a vector consisting of three objectives: maximization of Mn, and minimization of PDI and time. Polymer with higher Mn and lower PDI is the desired one that too in minimum possible time. Simultaneous solutions to these objectives are going to provide the high-quality product in optimum time as these objectives are conflicting in nature. In other words, more polymerization time is required to obtain high Mn. Also, as Mn increases, PDI has a tendency to increase as well. However, these objective functions with relevant constraints provide the desired polymer. Catalyst additions (C), Monomer addition (M), zeroth, first and second moment of dormant chain (OH end group) equations additions ($\mu 0$, $\mu 1$, $\mu 2$ respectively) and total polymerization time (t) are considered as decision variables.

All the decision variables are kept within the lower and upper bounds (min, max) that are chosen based on the experimental data from Yu et al. To avoid model extrapolation errors, the constraint bounds in the formulation were completely chosen based on these experimental values. The experimental values of PLLA PDI, for example, are around 2. Hence, 1.8 has been chosen as the constraint limit for the minimization process. Whereas higher the molecular weight the better the product. As a result, Mn greater than 40000 is chosen. Table 1 shows the MOOP formulation with constraints and decision variables ranges. The optimization routine determines these decision variables. By integrating the validated model with the optimization routine, the real coded NSGA II, MOOP was performed to obtain trade off solutions among the various conflicting objectives (Deb, 2001). Finding the globally optimum space of interest in this multidimensional search space is always difficult. NSGA II has hopefully resolved this difficult problem, which involves highly nonlinear stiff ordinary differential equations (ODE) with decision variables constrained by experimental observations.

Table 1: Multi objective optimization (MOOP) formulation

Maximize Mn

Minimize PDI

Minimize Time

$40000 \leq Mn$

$1 \leq PDI \leq 1.8$

$5000 \leq M/C \leq 20000$

$9 \leq ROH/C \leq 120$

$0.01\ h \leq time \leq 0.2\ h$

The values of decision variables:
$C^{min}=0.0008$ mol/l; $C^{max}=0.001$ mol/l
$M^{min}=4$ mol/l; $M^{max}=50$ mol/l
$\mu 0^{min}=0.0072$ mol/l; $\mu 0^{max}=0.15$ mol/l
$\mu 1^{min}=0.0072$ mol/l; $\mu 1^{max}=0.15$ mol/l
$\mu 2^{min}=0.0072$ mol/l; $\mu 2^{max}=0.15$ mol/l
$t^{min}=0.01$ h; $t^{max}=0.2$ h

3. Results and Discussion

Kinetic model for lactide ROP proposed in Yu et al have described the relationship between conversion vs Mn, Mw and PDI, time vs conversion, Mn, Mw and PDI vs conversion for different monomer/catalyst/co-catalyst ratio in temperature range 130-180 °C. Kinetic parameters for the model development have been estimated from the experimental data. This validated model was justified to formulate the MOOP.

Multi objective optimization with NSGA II for the MOOP formulation resulted in a set of PO solutions, as illustrated in Figure 2. This Pareto front is made up of solutions that are all competitive in the same way. As we go through the Pareto optimal solution, one objective improves in relation to the other. From these solutions, an operator or decision maker can choose one appropriate solution with respect to their intuition or by using higher-level information. Coello [10] and Cvetkovic and Parmee [11] have discussed the incorporation of preferences amongst Pareto optimal solutions. Optimized concentration profiles of monomer, catalyst and co-catalyst concentration corresponding to the specified objective function is shown in the figure 3. To obtain the unique result, a specific combination of these three reagents must be added. To analyse the lactide ROP under various conditions, two specific points are chosen from among the various PO solutions in the resulting pareto front, each with three different addition profiles for three different reagents and time. Table 2 shows these points as well as the validated model result.

In table 2, the validated model represents the obtained values of Mn, PDI, and time for the corresponding initial concentration of decision variables taken. MOOP point 1 represents the result of the pareto front, taking into account the minimum PDI. The corresponding Mn and time, as well as the quantity of the decision variables are also tabulated. Whereas MOOP point 2 represents the result of the pareto front, taking into account the maximum PDI. The corresponding Mn and time, as well as the quantity of the decision variables are also tabulated. The table clearly shows that as PDI decreases, Mn decreases proportionally. Similarly, the highest Mn is obtained with the highest PDI.

Table 2: Process performance analysis for different variables and objective function

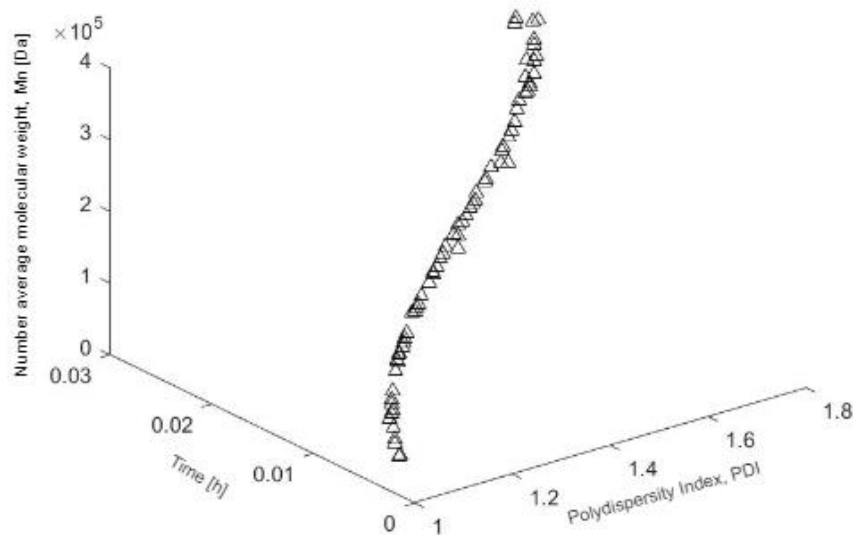|	Decision Variables				Objective Function		
	Monomer	Catalyst	Cocatalyst	Time [h]	Mn	PDI	Time [h]
Validated model	7.6	7.6×10^{-4}	0.0153	0.01	1.438×10^4	1.03	0.01
MOOP point 1	37.8	9.1×10^{-4}	0.071	0.0027	4.016×10^4	1.0256	0.0027
MOOP point 2	38.08	8.4×10^{-4}	0.083	0.0283	3.22×10^5	1.79	0.0283

Figure 2: Multi objective Pareto front plot for number average molecular weight, polydispersity index and polymerization time
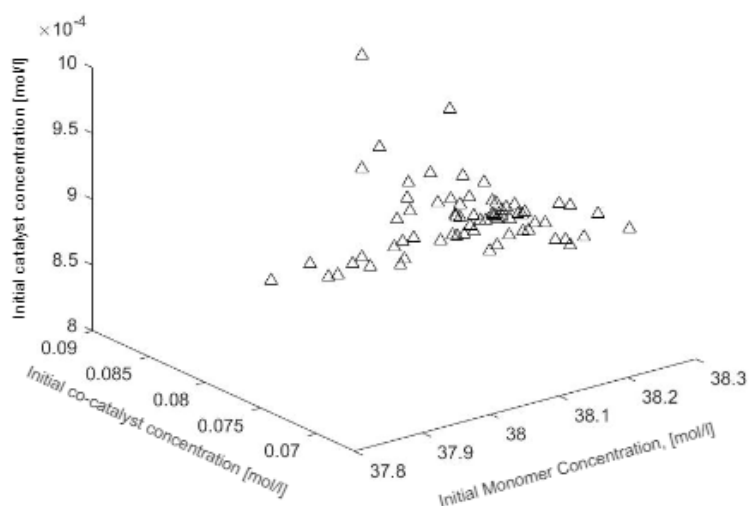
Figure 3: Multi objective Pareto front plot for monomer, catalyst, and co-catalyst

Figure 4 indicates the 2D plot of Mn vs time, and the polymerization appears to complete around 0.03 hour with maximum Mn up to around 3.3×10^5 Da for the MOOP formulation Whereas figure 5 indicates the 2D plot of Mn vs PDI, in which the PDI up to 1.8 provides maximum Mn of about 3.3×10^5 Da linearly. It shows that Mn increases as PDI increases, or that Mn and PDI are directly proportional. Mn and PDI both increase steadily over time, but their dynamics clearly vary according to the addition pattern. By considering the application, the operator can select the best PO solution. Meanwhile, the graph of Mn vs. time is skewed. Even though Mn tends to increase in the first few minutes, time is not entirely proportional to Mn. As time passes, the chances of transesterification and non-radical chain scission increase. Therefore , time and temperature should be kept at a minimum to slow down the chain scission of the growing chain. The developed kinetic model specifies the influence of all these side reactions. By solving the MOOP, we are achieving the best combination of additional reagent quantities for lactide ROP whilst also taking time and temperature into account.
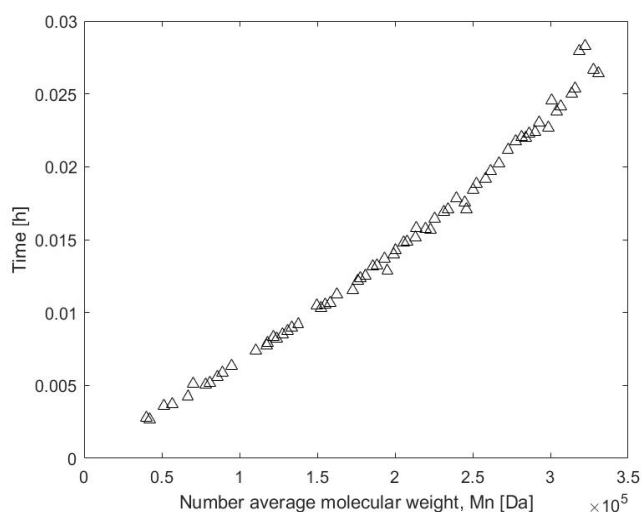

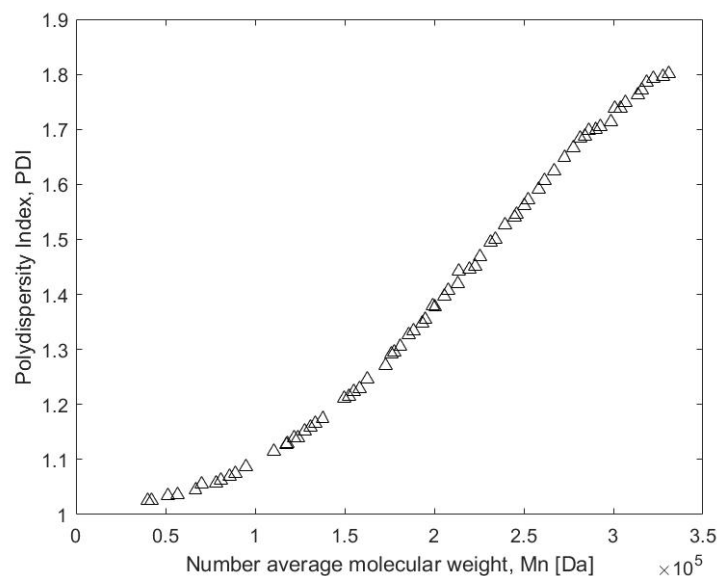Figure 4: Plot of the Number average molecular weight vs time

Figure 5: Plot of the Number average molecular weight vs polydispersity index

4. Conclusion

Elitist non-dominated sorting genetic algorithm (NSGA II) was used to perform multi-objective optimization of ROP of l-lactide using a well-validated moment-based kinetic model. A MOOP was formulated for conflicting objective functions, with the important properties of batch process l-lactide ROP in mind. The objective was to achieve the best possible results for the reagent addition patterns in terms of maximum Mn in the least amount of PDI and time with relevant constraints in the range of suitable decision variables. The optimization routine produced a wide range of solutions (pareto front) across the entire search space. When compared to existing data from the open literature, a significant number of solutions are found to be superior. Decision makers can choose the optimum operating conditions from this pareto optimal solution while maintaining the product quality. The distributions of various species have been studied, as well as their evolution over time. The profiles of various reagents are analysed as well as their relationships to the reaction mechanism. It also demonstrated the utility of NSGA II in these kinds of multidimensional nonconvex processes.

Acknowledgements

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