Mathematical Modeling for Continuous Reactive Extrusion of Poly Lactic Acid formation by Ring Opening Polymerization Considering Metal/Organic Catalyst and Alternative Energies

Satya P. Dubey, Hrushikesh A. Abhyankar, Veronica Marchante, James L. Brighton, Björn Bergmann

Abstract—PLA emerged as a promising polymer because of its property as a compostable, biodegradable thermoplastic made from renewable sources. PLA can be polymerized from monomers (Lactide or Lactic acid) obtained by fermentation processes from renewable sources such as corn starch or sugarcane. For PLA synthesis, ring opening polymerization (ROP) of Lactide monomer is one of the preferred methods. In the literature, the technique mainly developed for ROP of PLA is based on metal/bimetallic catalyst (Sn, Zn and Al) or other organic catalysts in suitable solvent. However, the PLA synthesized using such catalysts may contain trace elements of the catalyst which may cause toxicity. This work estimated the usefulness and drawbacks of using different catalysts as well as effect of alternative energies and future aspects for PLA production.

Keywords—Alternative energy, bio-degradable, metal catalyst, poly lactic acid (PLA), ring opening polymerization (ROP).

I. INTRODUCTION

THE production of large amount of waste is one of the major challenges at the present time, and polymers represent 70% of global waste [1]. Because of massive consumption, problems such as decomposition and recycling of the used polymers have been raised. As an alternative, bio-based and/or bio-degradable polymers such as cellulose acetate (CA), polyamide (PA), poly-butylene succinate (PBS), poly-lactic acid (PLA), poly-propylene (PP), poly-urethane (PU) etc. have raised interest [2]. PLA is a possible solution to these problems as it is compostable, biodegradable thermoplastic polymer made from renewable sources [3].

The conventional method of synthesis of PLA is ROP process based on metal (Sn, Al, Zn) catalysis of Lactide monomer using suitable co-catalyst such as dodecanol and solvent toluene, water etc. [3], [4], [1]. However, one of the main limitations for the application of PLA is the presence of traces of toxic metal catalyst in the final product. A safe and efficient production process needs to be developed to avoid potential hazards and toxicity. To overcome the issue of toxicity and health hazards, several groups have been investigating the production of PLA using non-metal/organic catalyst [5]-[9].

It has also been found that alternative energy sources (LASER, Ultrasounds, Microwaves) could be a prominent option to facilitate the ROP of lactide monomers [9]-[11].

The implementation of metal-free catalyst and suitable application of alternative energy source in the ROP of PLA may result in complete replacement of the metal catalysts from conventional process and production of considerable amount (128–152) kDa of PLA [12].

To overcome the issue of trace catalyst present in the final product while processing the ROP of PLA at commercial level, more safer and efficient mechanism is needed to produce PLA at large scale in environment friendly conditions.

The impact of activity of several metal/non-metal catalysts on the reaction mechanism of ROP of PLA was considered in this work. The state of the art of modelling several reaction mechanisms proposed in literature was done in chronological order. Based on investigation of kinetic model reported by [13]-[15] the most suitable mathematical models explaining the reaction mechanisms were modelled in the form of first order ordinary differential equations (ODE) to get the reaction output by comparing molecular weight and conversion with time. Matlab with RK-4 method was finalized for the mathematical modelling. The analysis of simulation model explains the impact of several reaction parameters like concentration, rate constants, time etc. significantly. To consider the scale of production at commercial level, the data created by mathematical model (variation of conversion rate and molecular weight with time and temperature) has been used in Ludovic® [21] software. The isothermal curves (data) generated as an output from the ODE is then used as input in Ludovic® software. Ludovic®, then uses the data to process actual extruder reaction conditions by considering the screw length, screw speed and viscosity parameter.

Satya P. Dubey, Research Scholar, and James L. Brighton, Senior Lecturer, are with the Centre for Automotive Technology, Cranfield University, UK (phone: +44(0)1234 75 2737); e-mail: s.p.dubey@cranfield.ac.uk, j.l.brighton@cranfield.ac.uk).

Hrushikesh A. Abhyankar is Research Fellow, Centre for Automotive Technology, Cranfield University, UK (phone: +44(0)1234 75 8085); e-mail: h.a.abhyankar@cranfield.ac.uk)

Veronica Marchante is Research Fellow, Centre for Automotive Technology, Cranfield University, UK (phone: +44(0)1234 75 8549); e-mail: v.marchanterodriguez@cranfield.ac.uk

Björn Bergmann is Research Scholar at Fraunhofer-Institutefür Chemische Technologie ICT, Germany (phone: +49 6151 155-9731); e-mail: Bjoern.Bergmann@ict.fraunhofer.de).

II. MATERIALS AND METHODS

A. Materials Details

ROP of lactide were performed at Fraunhofer, ICT lab [16]. As an initial test L-lactide monomer (Sigma-Aldrich) and stannous octoate $Sn(Oct)_2$ (Sigma-Aldrich) as catalyst to initiate the reaction process were mixed in the presence of tri-phenyl phosphine $(PPh)_3$ (Sigma-Aldrich), using toluene (Sigma-Aldrich) as solvent.

B. Experimental Process

The extrusion reaction was performed using a co-rotation twin screw extruder (Leistritz 27 HP). The extruder used has a diameter 27 mm and a length of 52 L/D. Ultrasound was applied with a specialized extruder block with the sonotrode being mounted at 25D (Ultrasound Sonification device UIP2000hdT, Hielscher Ultrasonics GmbH). Monomer and catalysts have been premixed under inert gas atmosphere and fed into main feed. To evaluate the influence of the rotation speed experiments have been conducted at 40, 75, 150, 300, 600 and 1000 rpm, while all remaining process parameters have been kept constant. The same initial conditions were used in all the cases, which are shown in Table I. In addition to optimize the reaction process of ROP of lactide through reactive extrusion, several tests were made. The details of experimental reaction parameters are mentioned in Table I.

TABLE I
REACTION PARAMETERS

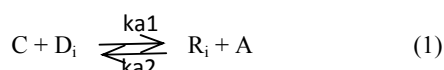| Symbol	PARAMETER	Value (Unit) [a]
M_0	Initial concentration of monomer	8.326 (mol/L)
C_0	Initial concentration of catalyst	0.008 (mol/L)
D_0	Initial concentration of co-catalyst	0.008 (mol/L)
T_0	Initial temperature	50 °C
M	Monomer mass	(1.2-2.5) $\dot{m}$ / kg/
RPM	Rotation speed	(40-1000) rotation/min

III. MATHEMATICAL MODELLING AND SIMULATION OF REACTION KINETICS OF ROP OF LACTIDE

The initial investigations provided satisfactory results compared to literature [13] but further detailed studies disclose the fact of several other reaction stages such as trans-esterification and chain scission. These two side reactions influence the molecular weight and conversion factor significantly.
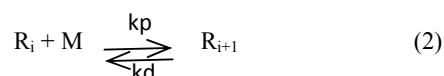
To overcome the issue of influence of side reaction on the output, reaction mechanism proposed by [15], [17] were investigated which consider all the relevant stages possible in the ROP of lactide by using $Sn(Oct)_2$ as a catalyst and 1-dodecanol as co-catalyst in the batch process.

The stages and reaction mechanism adopted is following:
Activation of catalyst:
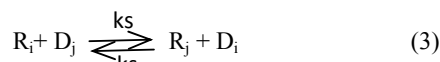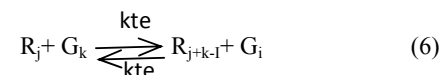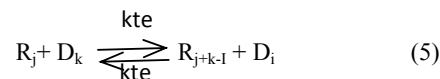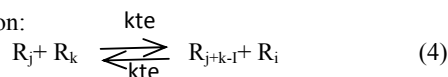
$$C + D_i \underset{ka2}{\overset{ka1}{\rightleftharpoons}} R_i + A \qquad (1)$$

Propagation:

$$R_i + M \underset{kd}{\overset{kp}{\rightleftharpoons}} R_{i+1} \qquad (2)$$

Chain transfer:

$$R_i + D_j \underset{ks}{\overset{ks}{\rightleftharpoons}} R_j + D_i \qquad (3)$$

Trans-esterification:

$$R_j + R_k \underset{kte}{\overset{kte}{\rightleftharpoons}} R_{j+k-I} + R_i \qquad (4)$$

$$R_j + D_k \underset{kte}{\overset{kte}{\rightleftharpoons}} R_{j+k-I} + D_i \qquad (5)$$

$$R_j + G_k \underset{kte}{\overset{kte}{\rightleftharpoons}} R_{j+k-I} + G_i \qquad (6)$$

Non-radical random chain scission:

$$R_j \xrightarrow{kde} R_{i-k} + G_k \qquad (7)$$

$$D_i \xrightarrow{kde} D_{i-k} + G_k \qquad (8)$$

$$G_i \xrightarrow{kde} G_{i-k} + G_k \qquad (9)$$

where: ka1, ka2: Activation rate coefficients, kp, kd: Propagation rate coefficients, ks: Chain-transfer rate coefficient, kte: Trans-esterification rate coefficient, kde: Random chain scission reaction rate coefficient.

C: catalyst, $Sn(Oct)_2$, A:octanoic acid (OctOH) produced by catalyst, R_i: Active polymer chain with length i, D_i: Dormant polymer chain with length i, G_i terminated polymer chain with length i, M monomer,

In the above proposed mechanism, reaction 1 represents the activation of catalyst (C), reaction 2 represents the propagation stage of monomer and reaction 3 signifies the chain termination part of the reaction. The reactions 4-6 are side reactions known as intermolecular trans-esterification. Similarly reactions 7-9 are side reaction called Non-radical random chain scission which mostly occurs at higher reaction temperatures.

In order to model the above reaction mechanism, reaction stages 1-9 were transformed into first order ordinary differential equations. The differential equations were designed to consider the influence of each reaction parameter such as rate constants, concentration variation with time and concentration of catalyst, co-catalyst and Lactide monomer.

C. Mathematical Modelling of Reaction Mechanism

The Mathematical format of the reaction mechanism is following:

$$\frac{d[C]}{dt} = -ka1 \cdot [C] \cdot \sum_{i=1}^{n}[D_i] + ka2 \cdot \sum_{i=1}^{n}[R_i] \cdot [A] \qquad (10)$$

$$\frac{d[A]}{dt} = ka1 \cdot [C] \cdot \sum_{i=1}^{n}[D_i] - ka2 \cdot \sum_{i=1}^{n}[R_i] \cdot [A] \qquad (11)$$

$$\frac{d[M]}{dt} = -kp \cdot [M] \cdot \sum_{i=1}^{n}[R_i] + kd \cdot \sum_{i+1}^{n}[R_j] \qquad (12)$$

$$\frac{d[R_i]}{dt} = ka1 \cdot [C] \cdot [D_i] - ka2 \cdot [R_i] \cdot [A] - kp \cdot [M] \cdot [R_i] + kd \cdot [R_{i+1}] + kp \cdot [M] \cdot [R_{i-1}] - kd \cdot [R_i] - ks \cdot [R_i] \cdot \sum_1^n [D_j] + ks \cdot [D_i] \cdot \sum_1^n [R_j] - kte \cdot [R_i] \cdot \left(\sum_1^n [R_j] + \sum_1^n [D_j] + \sum_1^n [G_j] \right) + kte \cdot \sum_{\substack{j=1 \\ j+k>i}}^n [R_j] \cdot \left(\sum_{\substack{k=1 \\ j+k>i}}^n [R_k] + \sum_{\substack{k=1 \\ j+k>i}}^n [D_k] + \sum_{\substack{k=1 \\ j+k>i}}^n [G_k] \right) - kde \cdot i \cdot [R_i] + kde \sum_{i+1}^n [R_j] \quad (13)$$

$$\frac{d[D_i]}{dt} = -ka1 \cdot [C] \cdot [D_i] + ka2 \cdot [R_i] \cdot [A] + ks \cdot [R_i] \cdot \sum_1^n [D_j] - ks \cdot [D_i] \cdot \sum_1^n [R_j] - kte \cdot [D_i] \cdot \sum_1^n [R_j] + kte \cdot \sum_{\substack{j=1 \\ j+k>i}}^n [R_j] \cdot \sum_{\substack{k=1 \\ j+k>i}}^n [D_k] - kde \cdot i \cdot [D_i] + kde \cdot \sum_{i+1}^n [D_j] \quad (14)$$

$$\frac{d[G_i]}{dt} = -kte \cdot [G_i] \cdot \sum_1^n [R_j] + kte \cdot \sum_{\substack{j=1 \\ j+k>i}}^n [R_j] \cdot \sum_{\substack{k=1 \\ j+k>i}}^n [G_k] - kde \cdot i \cdot [G_i] + kde \cdot \left(\sum_{i+1}^n [R_j] + \sum_{i+1}^n [D_j] + \sum_{i+1}^n [Gj] \right) \quad (15)$$

ODES (10-15) were solved using MATLAB – RungeKutta– 4 method.

To calculate the number average molecular weight $(\overline{M_n})$ (17) and Conversion factor (X) (16) following expressions were defined:

$$X = 1 - \frac{[M]}{[M_0]} \quad (16)$$

$$\overline{M_n} = \frac{[M_0] X}{[R_T] + [D_T]} m_{mon} \quad (17)$$

where *[M] & [M₀]* are the concentration of monomer; *[R_T]:* Summation of all the active chain species $(\sum_0^n R_i)$; *[D_T]:* Summation of all the dormant chain species $(\sum_0^n D_i)$; m_{mon}: The molecular weight of lactide monomer

IV. MODELLING OF PLA REACTION MECHANISM IN REACTIVE EXTRUSION

In order to explain the effect of flow of material and mixing with several materials (catalyst & cocatalyst) in the extrusion reaction at higher scale, theoretical large scale simulation were performed by Ludovic® software [21]. To investigate the mechanism of ROP of lactide in the compartment flow extruder, in Ludovic®, the whole extruder were divided into several zones. The proper mixing of the materials in the extruder at several zones plays significant role in obtaining optimum output.

To perform the large scale simulation process through Ludovic®, initial data such as rate kinetics, temperature variation and variation of $\overline{M_n}$ and X with time were provided by above developed mathematical model (Heading *C*) based on batch process and solved with the help of Matlab RungeKutta-4 method. The parameters which are crucial and backbone of Ludovic® software to simulate extrusion reaction are isothermal curves which show variation of $\overline{M_n}$ vs time (t) and conversion(X) vs time(t) at different temperatures. These details are needed to get the idea of thermodynamic behaviour of reaction at several stages. The variation provides the trend of change of product as reaction proceeds through extruder.

D. Mechanism of Extruder Reaction through Ludovic®

Ludovic® reproduces the thermo-mechanical behaviour of twin screw extruders [14]. It deals with the parameters which directly affect the reaction output such as residence time of mixed material, rate constants, viscosity and thermo-mechanical flow.

The geometry of the extruder which considers the rotation speed of the screw, throughput and melt flow affect the mechanical energy which will create an impact on thermal response of the material. References [10], [11], [18]-[20] reported that alternative energy sources (LASER, Ultrasounds, Microwaves) could be a prominent option to facilitate the ROP of Lactide. The implementation of metal-free catalyst and suitable application of alternative energy source in the ROP of lactide may result in complete replacement of the metal catalysts from the conventional method and production of considerable amount (128–152) kDa of PLA.

V. RESULTS

E. Experimental Data

Experimental data of average residence time (tR), temperature (T), number average molecular weight $(\overline{M_n})$ and average molecular weight $(\overline{M_w})$ obtained using L-lactide as monomer, stannous octoate Sn(Oct)₂ as catalyst and tri-phenyl phosphine (PPh)₃ as co-catalyst through reactive extrusion process using and not using ultrasounds for initial mixing are provided in Table II. The values of conversion and molecular weight distribution were characterized by size exclusion chromatography (GPC). It can be observed that the increase in temperature results in an increase in $\overline{M_n}$ and $\overline{M_w}$ for the same initial conditions. But also, $\overline{M_n}$ and $\overline{M_w}$ increase when ultrasound is applied. In addition, for the experiments at 190 °C the conversion when ultrasounds are applied (80%) is higher than without ultrasound (58%).Therefore, the initial step of mixing monomer and catalyst with ultrasounds boosts/improves the performance of the reactive extrusion.

TABLE II
EXPERIMENTAL DATA

t_R(min)	T(°C)	Ultrasound	$\overline{M_n}$[kDa]	$\overline{M_w}$ [kDa]
2.30	190	Yes	12.4	15.5
		No	77.2	10.6
6.10	200	Yes	14.8	20.2
		No	13.5	17.6
7.30	205	Yes	30.1	50.0
		No	13.7	18.4

F. Results of Simulation in Batch Process

Based on experimental parameters and initial conditions, mathematical simulation was performed for a total reaction time of (0-8) min and temperature range of 190-205 °C. The results are presented in Table III, including temperature (T), number average molecular weight $(\overline{M_n})$ and average molecular weight $(\overline{M_w})$.

In this case, the increase of the reaction temperature favours the growth of the polymer chain. This is manifested in an increase in $\overline{M_n}$ and $\overline{M_w}$. The calculated value of $\overline{M_n}$ and

$\overline{M_w}$ reported slightly higher than the experimental results obtained during reactive extrusion, but the trend is similar. On the other hand, the rates of conversion obtained in the simulated processes are close to the total conversion (around 99.0%) at very large time and temperature but these results are based on the modelling of a batch process, in which it is assumed a situation of perfect mixture.

TABLE III
SIMULATION DATA

t(min)	T(°C)	$\overline{M_n}$ [kDa]	$\overline{M_w}$ [kDa]
2.30	190	8.5	12.7
6.10	200	31.1	45.4
7.30	205	35.0	52.2

VI. DISCUSSION

The ROP process for PLA production using ultrasound as one of the alternative energy sources in the twin screw extruder depends on several factors such as temperature influence, throughput influence, screw rotation speed etc. For the proper polymerization process of Lactide, mixing has proven to be one of the crucial factors. The impact of extruder configuration and design affects the procedure and output of PLA significantly. The design of several mixing chambers within the extruder and the speed of twin screw influence the propagation rate of PLA synthesis [14].

When investigating the rotation speed dependent energy incorporation, interestingly the energy curves for 40, 75 and 150 rpm are nearly equal, while the energy incorporated at 600 and 1000 rpm is nearly equal as well, but much higher as for the lower rotation speeds. The temperature range varies from 160 to220 °C while in case of screw rotation speed it varies from (40-600) rpm. In case of throughput, it varies from 0.5 to 2.5 kg/h. In reactive extrusion process the configuration of screw and extruders affects the polymerization significantly [14].

The effect of ultrasound source combined with above changes is following:

- Ultrasounds enables polymerization at low rotation speed
- Ultrasound seems to improve polymerization at medium rotation speed
- Ultrasound effect on high rotation speed 100 rpm not visible
- Ultrasound accelerates the polymerization of the lactide.
- The heating effect which is a side effect of the sonication treatments seems to influence the polymerization positively

The result mentioned in Table II shows positive impact of AE source on reaction mechanism. At large time and higher temperature in the presence of AE source, the values of $\overline{M_n}$ and $\overline{M_w}$ are high. Similar effect also reported in Table III, the data calculated through mathematical simulation. Further on to perform the simulation considering reactive extruder condition, the simulation data obtained by batch process will be used as an input for Ludovic® software which calculates the final result of the continuous reactive extrusion process and compared with experimental result to facilitate reaction parameter details for the production of PLA at commercial level.

VII. CONCLUSION

For the production of safe and effective PLA polymer from lab scale to industrial scale, further investigations will be required which includes large scale computational simulation. Research which involves the experimental and theoretical investigation of PLA synthesis considering metal free catalysts and alternative energy in the reaction seems to be an effective mechanism to focus on. Theoretical modelling and simulation are useful to provide an estimate of the throughput and help to plan the experimental/industrial production accordingly. The results obtained through theoretical simulation such as information regarding rate kinetics, concentration variation, viscosity change and temperature influence on rate constants are the key parameter for prediction of large scale production of PLA by reactive extrusion process applying Ludovic® simulator [22]. Data created by Ludovic® will help the experimental setup getting more productive and precise output.

The initial experimental tests of ROP of lactide in reactive extrusion process shows that the application of AE can improve the performance of the reaction. It was proven that the application of ultrasounds boosts the growth of polymer chains.

In addition, the simulation of the batch process describes closely the results obtained experimentally. The mathematical model can be implemented in Ludovic® software to simulate and optimise a reactive extrusion process. This can be done by implementing isothermal curves for the conversion and number average molecular weight in Ludovic® software. Currently, this stage is in under development.

Groups such as InnoREX consortium (www.InnoREX.eu) [9] are performing detailed step by step investigations of above defined mechanism to achieve highly precise, controlled and large scale synthesis of PLA by reactive extrusion process. The group is working on replacing the metal catalysts as well as on implementation of AE sources in the reaction process. To achieve this target, lab scale experiments and mathematical simulation models to verify the output of the reaction are in progress. To consider the impact of AE sources and to study the production quality/market demands of PLA (Medical, Electronic & Food Packaging), several industrial partners also involved in InnoREX group. For the production of PLA through continuous, highly precise and controlled metal-free polymerization process, not only the InnoREX group but many other experts from industries like Purac [22] and NatureWorks [23] also involved to investigate and develop innovative method.

(SCC)-France, Fraunhofer.-ICT and other partners from www.InnoREX.eu group by providing details of the investigation of PLA research.

REFERENCES

[1] S. Jacobsen, H.-G. Fritz, P.Degée, P.Dubois, and R.Jérôme, "Continuous reactive extrusion polymerisation of L-lactide ― an engineering view," Macromol. Symp., vol. 153, no. 1, pp. 261–273, 2000.

[2] K. Madhavan Nampoothiri, N. R. Nair, and R. P. John, "An overview of the recent developments in polylactide (PLA) research," Bioresour. Technol., vol. 101, no. 22, pp. 8493–8501, Nov. 2010.

[3] P. Dubois, C. Jacobs, R. Jerome, and P. Teyssie, "Macromolecular engineering of polylactones and polylactides. 4. Mechanism and kinetics of lactide homopolymerization by aluminum isopropoxide," Macromolecules, vol. 24, no. 9, pp. 2266–2270, Apr. 1991.

[4] D. R. Witzke, R. Narayan, and J. J. Kolstad, "Reversible Kinetics and Thermodynamics of the Homopolymerization of l-Lactide with 2-Ethylhexanoic Acid Tin(II) Salt," Macromolecules, vol. 30, no. 23, pp. 7075–7085, Nov. 1997.

[5] N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, and J. L. Hedrick, "Organocatalytic ring-opening polymerization," Chem. Rev., vol. 107, no. 12, pp. 5813–5840, 2007.

[6] W. Jeong, J. L. Hedrick, and R. M. Waymouth, "Organic Spirocyclic Initiators for the Ring-Expansion Polymerization of β-Lactones," J. Am. Chem. Soc., vol. 129, no. 27, pp. 8414–8415, Jul. 2007.

[7] M. Myers, E. F. Connor, T. Glauser, A. Möck, G. Nyce, and J. L. Hedrick, "Phosphines: Nucleophilic organic catalysts for the controlled ring-opening polymerization of lactides," J. Polym. Sci. Part Polym. Chem., vol. 40, no. 7, pp. 844–851, Apr. 2002.

[8] I. Başaran and A. Oral, "Synthesis and Characterization of Poly(L-Lactic acid)/Clay Nanocomposite via Metal-Free Process," Polym.-Plast. Technol. Eng., vol. 52, no. 12, pp. 1271–1276, 2013.

[9] "InnoREX." (Online). Available: http://www.innorex.eu/about.php.

[10] S. Jing, W. Peng, Z. Tong, and Z. Baoxiu, "Microwave-irradiated ring-opening polymerization of D,L-lactide under atmosphere," J. Appl. Polym. Sci., vol. 100, no. 3, pp. 2244–2247, May 2006.

[11] P. Albert, H. Warth, R. Mülhaupt, and R. Janda, "Comparison of thermal and microwave-activated polymerization of ε-caprolactone with titanium tetrabutylate as catalyst," Macromol. Chem. Phys., vol. 197, no. 5, pp. 1633–1641, May 1996.

[12] A. Södergård and M. Stolt, "Industrial Production of High Molecular Weight Poly(Lactic Acid)," in Poly(Lactic Acid), R. Auras, L.-T. Lim, S. E. M. Selke, and H. Tsuji, Eds. John Wiley & Sons, Inc., 2010, pp. 27–41.

[13] R. Mehta, V. Kumar, and S. N. Upadhyay, "Mathematical Modeling of the Poly(lactic acid) Ring–Opening Polymerization Kinetics," Polym.-Plast. Technol. Eng., vol. 46, no. 3, pp. 257–264, 2007.

[14] I. Banu, J.-P. Puaux, G. Bozga, and I. Nagy, "Modeling of L-lactide Polymerization by Reactive Extrusion," Macromol. Symp., vol. 289, no. 1, pp. 108–118, 2010.

[15] Y. Yu, G. Storti, and M. Morbidelli, "Ring-Opening Polymerization of l,l-Lactide: Kinetic and Modeling Study," Macromolecules, vol. 42, no. 21, pp. 8187–8197, Nov. 2009.

[16] "Compounding and extrusion - Fraunhofer ICT." (Online). Available: http://www.ict.fraunhofer.de/en/comp/pe/ce.html.

[17] Y. Yu, G. Storti, and M. Morbidelli, "Kinetics of Ring-Opening Polymerization of l,l-Lactide," Ind. Eng. Chem. Res., vol. 50, no. 13, pp. 7927–7940, Jul. 2011.

[18] L. J. Liu, C. Zhang, L. Q. Liao, X. L. Wang, and R. X. Zhuo, "Microwave-assisted Polymerization of D, L-Lactide with Stannous Octanoate as Catalyst," Chin. Chem. Lett., vol. 12, no. 8, pp. 663–664, 2001.

[19] M. Vukomanović, M. Mitrić, S. D. Škapin, E. Žagar, J. Plavec, N. Ignjatović, and D. Uskoković, "Influence of ultrasonic processing on the macromolecular properties of poly (d,l-lactide-co-glycolide) alone and in its biocomposite with hydroxyapatite," Ultrason. Sonochem., vol. 17, no. 5, pp. 902–908, Jun. 2010.

[20] C. Zhang, L. Liao, and L. Liu, "Rapid Ring-Opening Polymerization of D,L-Lactide by Microwaves," Macromol. Rapid Commun., vol. 25, no. 15, pp. 1402–1405, Aug. 2004.

[21] "Ludovic - Twin screw extrusion - SCConsultants." (Online). Available: http://www.scconsultants.com/en/ludovic-twin-screw-simulation-software.html..

[22] "Purac home." (Online). Available: http://www.purac.com/.

[23] "NatureWorks LLC Home Page." (Online). Available: http://www.natureworksllc.com/.