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Modeling of L-lactide Polymerization by Reactive Extrusion

Ionut Banu,[1,2] *Jean-Pierre Puaux,**[2] *Grigore Bozga,*[1] *Iosif Nagy*[1]

The kinetics of L-lactide ring-opening polymerization initiated by stannous octoate and triphenylphosphine was investigated in a batch apparatus (Haake Rheocord Mixer). Based on the experimental data, a kinetic model is developed, considering a coordination-insertion mechanism. Reactive extrusion experiments were further conducted for the same polymerization process, on a co-rotating twin screw extruder. The melted material flow and mixing was described by using the Ludovic® commercial simulator. Based on the developed kinetic model and simulated flow of L-lactide polymerization mixture, a mathematical model of reactive extrusion process is formulated, describing the evolutions of monomer conversion and average molecular weight along the extruder. The model is predicting with a reasonable good accuracy the experimental data.

Keywords: L-lactide polymerization; reactive extrusion modeling

Introduction

The polylactides are biodegradable and biocompatible polymers used in medical applications or as packaging material.[1] The polymer can be prepared by two ways, the first starting from lactic acid as raw material by polycondensation and the second using as monomer the lactic acid dimer (lactide) by ring-opening polymerization.[2] The second route produces high-molecular weight polymers using an appropriate initiator.[3] Stannous octoate[4] and an equimolecular mixture of stannous octoate and triphenyl phosphine [5,6] are used in the published studies as efficient initiation systems. At the best of our knowledge, there are only few studies in the published literature concerning modeling of L-lactide ring-opening polymerization. Witzke et al.[7] considered a reversible propagation process and studied the process thermodynamics, proposing a value for the activation energy of this elementary step. Mehta et al.[8,9] proposed a kinetic model and determined the values of the corresponding kinetic parameters, by using published data. One of our previous studies presents also a modeling study for L-lactide ring-opening polymerization initiated by stannous octoate.[10]

The twin screw extruder can be considered as a particular type of tubular reactor. A polymerization process can be performed by reactive extrusion only if reaction time is of the same magnitude order as the mean residence time in the twin-screw extruders. A study of reactive extrusion of L-lactide initiated by stannous octoate/triphenyl phosphine was performed by Jacobsen et al.[3,6] and the influence of the operating parameters on the polymer characteristics at the extruder outlet was discussed. Modeling approaches for this reactive extrusion process was not reported in the mentioned papers.

The complexity of the flow in twin-screw extruders, as well as the large number of parameters and interrelated variables affecting the flow, make the reactive extrusion process difficult to understand, describe, control and optimize. Besides the

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[1] University Politehnica of Bucharest, 313 Spl. Independentei, sector 6, 060042 Bucharest (Romania)
[2] Université Claude Bernard - Lyon 1, 69622 Villeurbanne cedex (France)
E-mail: puaux@univ-lyon1.fr

process kinetics, other important elements in the process modeling are the material flow and mixing. The flow of the polymer melts in the twin screw extruder can be studied using two approaches.[11,12] The first one is based on a local description of the flow field (and requires the development of the flow equations for a complex geometry in three-dimensional space). The second one, largely used in the study the material flow and mixing in chemical apparatus, is based on the concept of flow model and measurements of residence time distribution (RTD).[13]

The objective of this work is to develop a mathematical model for the L-lactide polymerization process in a twin-screw extruder. In this aim, experimental studies were carried out in order to investigate both the process kinetics and the performances of PLA synthesis process by reactive extrusion. Due to the lack of an adequate tracer for PLA flowing material, the RTD of L-lactide polymerization system was estimated by the Ludovic® software. This simulation environment is a computer software developed by Vergnes et al.[12] used to describe the flow in a twin-screw extruder.

A mathematical model of the isothermal reactive extrusion process was further developed based on the kinetics and RTD so determined. The comparisons of simulated and measured reactive extrusion results showed a fairly good quality of the modeling procedure.

Kinetic study

Materials and method

The L-lactide dimer was purchased from Boehringer Ingelheim and the Stannous Octoate (Sn-bis-ethyl-2-hexanoate, $SnOct_2$) and Triphenylphosphine (TPP) initiators from Sigma Chemicals. The aim is to investigate the process characteristics in the commercial purity conditions of the lactide and initiating mixture. Consequently, both the L-lactide dimmer, stannous octoate and triphenilphosphine initiator were used as received, without any treatment.

L-lactide polymerization experiments were performed in a HAAKE Rheocord mixer at temperature and shear rates values specific for the working conditions inside a twin-screw extruder. Temperatures in the range of 185–205 °C and a screw speed of 50 rpm were used in the kinetic experiments. The total mass of the sample is 50 grams. The maximum reaction time used for each experiment is 30 min. The experiments are performed for two values of monomer to initiator (M/I) ratio, 2250 and 4500, respectively. An equimolecular mixture of stannous octoate and triphenylphosphine is used as initiation mixture. For a better control of the initiator quantity, it was previously dissolved in anhydrous toluene, then the corresponding quantity was mixed with the monomer and feed in the Haake mixer.

In order to extract composition samples from the molten reaction mixture (the sampling time was 5 minutes), the device screws were stopped for about 5 seconds for each sample. The sample was immediately cooled in a current of cold air and then stored in a refrigerating space, before to be sent for analysis.

Polymer Characterization

Time dependencies of monomer conversion and average molecular weights were measured at different temperatures and molecular monomer to initiator ratios. The monomer conversions were determined based on proton nuclear magnetic resonance (^{1}H-NMR) spectra and the molecular weights by size exclusion chromatography (SEC) method.

The ^{1}H-NMR analyses were performed in deuterated chloroform at 25 °C, using a Bruker 250 instrument. A number of 128 scans were performed for each sample, until the complete separation for the characteristic frequencies for polymer and monomer. The measurement of monomer concentration was performed by ^{1}H-NMR spectroscopy analysis of reaction mixture, from integration between methine quartets of monomer ($\delta CH_{L\text{-}LA} = 5.01$ ppm) and those of the polymer ($\delta CH_{PL\text{-}LA} = 5.14$ ppm).[14–16]

The SEC measurements have been performed at 30 °C using chloroform as solvent and a solution of 5 mg/ml of L-lactide, on a Waters 510 apparatus using a Polymer Laboratory PLGel 5 μm Mixed-C column. The detector was a Waters 410 differential refractometer, and the scaling has been made using polystyrene standards provided by PolymerLab. A flow rate of 1 mL/min (total time of 12 minutes) was used for each analysis. The method was used to determine the molecular weight distribution and the mean-molecular weights of the polymers.

Kinetic Modeling

Following the approach developed in one of our previous studies,[10] a simplified scheme is used to describe the kinetics of the L-lactide ring-opening polymerization initiated by an equimolecular mixture of stannous octoate and triphenylphosphine ($SnOct_2$/TPP). The reaction rate expressions involve reaction rate constants for the main elementary steps: initiation (k_i), propagation (k_p), chain transfer to monomer (k_{tm}), and chain transfer to impurities present in the mixture (k_{ts}).

Using the experimental data and the batch polymerization mathematical model the kinetic parameters k_i, k_p, k_{tm}, and k_{ts} were determined by the least squares method. The calculated values are presented in Table 1. Several calculated values of monomer conversion and average molecular weight, for three representative experiments, are presented comparatively with measured data in Figure 1.

The value of the activation energy for the propagation step (91.1 kJ/mol) is in the same range to those reported by other authors (80 kJ/kmol reported by Eenink,[4] 70.9 kJ/kmol by Witzke et al.[7] and 86.2 kJ/kmol by Ryner et al. [17]).

Reactive Extrusion Experiments

Polymerization experiments were performed in a co-rotating twin-screw extruder (Leistritz LSM 30-34) with the following characteristics: barrel length, L = 1.2 m; centerline distance, CL = 30 mm, screw external diameter, D = 34 mm and the length to diameter ratio, L/D = 35. The barrel is divided into ten equivalent sections, each one equipped with an electrical resistance for heating and a water cooling system, both used to insure an independent control of the temperature. The screw profile is presented in Figure 2. In the reactive extrusion experiments, the temperature was 200 °C, the flow rates between 0.75 and 1.5 kg/h, and the screw speeds in the interval 50–300 rpm. The necessary amounts of stannous octoate and triphenyl phosphine were dissolved in anhydrous toluene and the resulted solution was manually mixed with the corresponding quantity of monomer in a plastic bag. The mixture was then fed into the extruder using a K-tron gravimetric feeder and the extrusion process was started. After a stabilization time of approximately 10 min, the polymer samples were taken in small aluminium recipients, cooled in a current of cold air and then hermetically closed into plastic bags and stored in a refrigerator, to be sent for analysis. The results obtained in the operating conditions used in this paper,

Table 1.
Calculated kinetic parameters values

Parameter	$\overline{k_i}$, $l \cdot mol^{-1}\,\min^{-1}$	$\overline{k_p}$, $l \cdot mol^{-1}\,\min^{-1}$	$\overline{k_{tm}}$, $l \cdot mol^{-1}\,\min^{-1}$	$\overline{k_{ts}}$, $l \cdot mol^{-1}\,\min^{-1}$
Values	1.279×10^1	5.53×10^1	6.99×10^{-2}	2.05×10^1
Parameter	E_i, $J \cdot mol^{-1}$	E_p, $J \cdot mol^{-1}$	E_{tm}, $J \cdot mol^{-1}$	E_{ts}, $J \cdot mol^{-1}$
Values	5.46×10^4	9.11×10^4	7.65×10^4	1.06×10^5

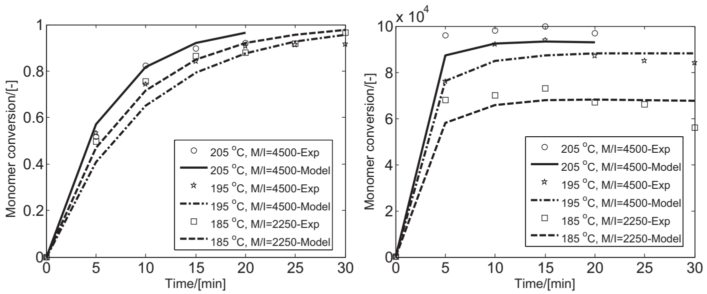

Figure 1.
Calculated vs. experimental monomer conversion (left) and number average molecular weight (right)

in terms of monomer conversion and average molecular weights are given in Table 7.

Modeling of the PLA Flow in a Twin-Screw Extruder

In order to describe the flow and mixing of the reaction mixture along the screw, we used the simulations performed by Ludovic® software. Based on the simulated results, we adapted two classical flow models to the PLA extrusion process, the axial dispersion model (AD) [13] and a compartment type model.

The Pe parameter of the axial dispersion model was calculated directly from the simulated RTD data.

The compartment type model is assuming that the filled sections (mainly the kneading disks zones), where the mixing is important, are perfectly mixed, while the partially filled transport sections are of plug flow type. Since a direct RTD measurement tracer was not available, we used a calculated RTD obtained by the flow simulated using the Ludovic® simulation package. This gives the filing ratios of the different sections, and the local residence times, as well as the global RTD curve. In order to evaluate the ability of Ludovic® package to predict the residence time distribution of the polymer flow, a test was carried out on polypropylene (PP) as flowing material.

Test of Ludovic® Simulator by Polypropylene Extrusion Experiments

The experimental work on the polypropylene (PP) RTD measurement is based on the use of hydroxymethyl anthracene tracer (as a dispersion in polypropylene) developed by Cassagnau et al. [18,19], combined with an UV spectroscopic method to detect its concentration in the melted propylene at the extruder exit. The RTD experiments were performed on the screw profile in Figure 1 at flow rates of 0.75–1.5 kg/h, a temperature of 200 °C and screw speeds of 50 to 300 rpm. Experimentally determined RTD curves for representative operating conditions are presented in Figure 3.

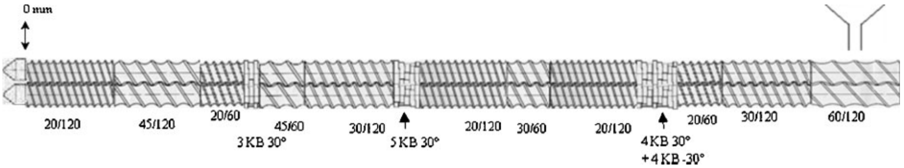

Figure 2.
Screw profile

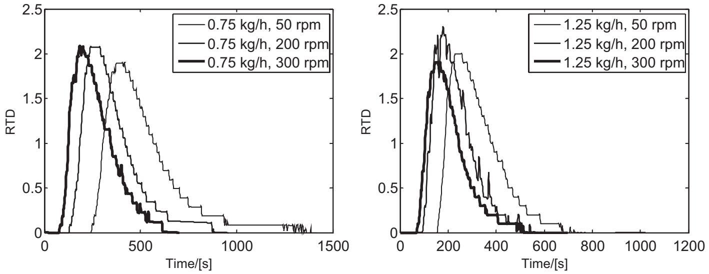

Figure 3.
Residence time distribution curves for polypropylene flow

The mean residence time and the residence time dispersion values determined from the experimental curves are presented in Table 3. As expected, a decrease of residence time with the increase of the screw speed of the flow rate can be observed from these data.

The simulations were performed in similar working conditions as for PLA synthesis, using a barrel temperature of 200 °C and the screw configuration presented in Figure 1. The rheological properties of the material were experimentally evaluated using an RMS800 rheometer for a sample of polypropylene and fitted on a Carreau-Yasuda viscosity model:

$$\eta = \eta_0 (1 + (\lambda \dot{\gamma})^a)^{\frac{m-1}{a}} \tag{1}$$

Figure 4 shows an excellent adequacy of the Carreau-Yasuda viscosity model in fitting the experimental rheological values for PP. The parameters of the Carreau-Yasuda model defined by equation (1) are given in Table 2. The calculations were performed by approximating a constant averaged viscosity along the TSE.

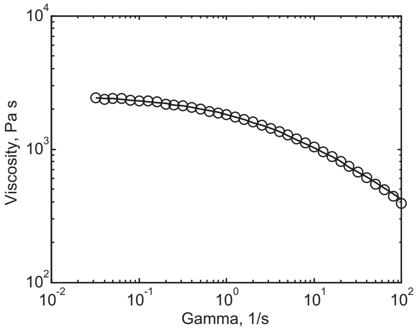

Figure 4.
Experimental (points) and calculated (solid) values of polypropylene viscosity

An example of RTD curve simulated with Ludovic® is presented in Figure 5 for a flow rate of 0.75 kg/h and a screw speed of 50 rpm.

The simulation results for the polypropylene flow on the screw configuration of the extruder are presented comparatively with the measured ones in Table 3. From the data given in this table, a fairly good agreement between experimental and simulated data can be observed. As seen, the quality of the mean residence time predictions is improving with the increase of the screw speed.

The results presented above prove a relatively good capability of Ludovic® simulator to predict both $\bar{t}$ and σ_t^2 of the polymer flow in the twin screw extruder used in PLA synthesis. The average errors between the calculated and experimental values were of 9.5% for mean residence time and 14.5% for σ_t^2. This can be an argument for using the Ludovic® simulated RTD curves in the modeling of L-lactide polymerization process by reactive extrusion.

Table 2.
Carreau-Yasuda parameters for PP model

Model	η_0	λ	a	m
1	2.549×10^3	3.301×10^{-1}	5.938×10^{-1}	5.100×10^{-1}

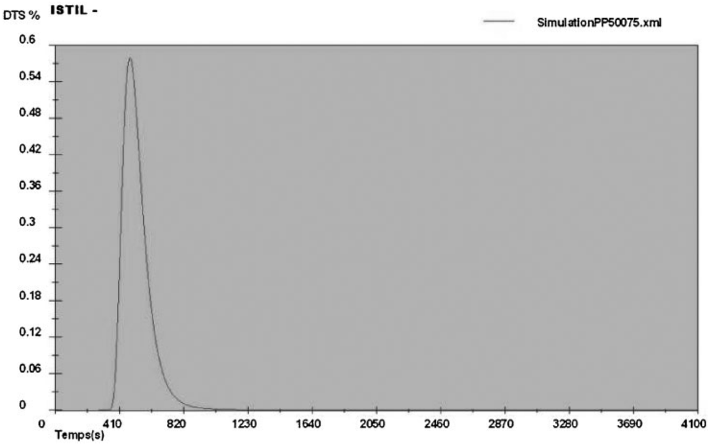

Figure 5.
Simulated RTD curve for PP flow in TSE: 0.75 kg/h, 50 rpm

Table 3.
Experimental and simulated residence times at 200 °C

Experience	Mass flow rate, [kg/h]	Screw speed, [rpm]	$\bar{t}$/[min], Experimental	$\bar{t}$/[min], Ludovic	σ_t^2 Experimental	σ_t^2 Ludovic
1	0.75	50	7.44	8.26	0.1136	0.1142
2	0.75	200	4.94	4.20	0.1697	0.2174
3	0.75	300	3.75	4.03	0.2247	0.2257
4	1.25	200	3.32	2.78	0.2599	0.3270
5	1.25	300	2.61	2.58	0.2918	0.3518
6	1.50	200	2.55	2.44	0.3350	0.3751
7	1.50	300	2.49	2.22	0.3486	0.4093

$\bar{t}$- mean residence time, σ_t^2 – variance of the RTD

Flow Simulation by Ludovic® Software for PLA Reactive Extrusion

The software needs some data relative to the material, including viscosity models for the reaction mixture. The PLA viscosity data were taken from the published literature [21] and fitted on a Carreau-Yasuda viscosity model (relation (1)). The calculated parameters of the viscosity equation (η_0, λ, m and a) are given in Table 4 and a comparison of the predicted values with the published values of polymer viscosity is presented in Figure 6.

Once provided the data concerning the structure of screw profile, screw speed, feed rate and viscosities, the Ludovic® software is able to calculate the pressures, temperatures, filing ratio profiles, local and global residence times. The calculations were performed approximating a constant averaged viscosity along the TSE.

Mathematical Modeling of PLA Reactive Extrusion by Axial Dispersion (AD) Model

The values of Pe number were calculated by fitting the RTD curves of axial dispersion model and simulated RTD respectively. The results are given in Table 5.

The mathematical model of the extrusion process, corresponding to the AD hypothesis

Table 4.
Estimated values for the parameters of the Carreau-Yasuda viscosity model

Model	η_0	λ	a	m	M_w
1	7.118×10^3	1.133×10^{-1}	9.033×10^{-1}	5.100×10^{-1}	130000

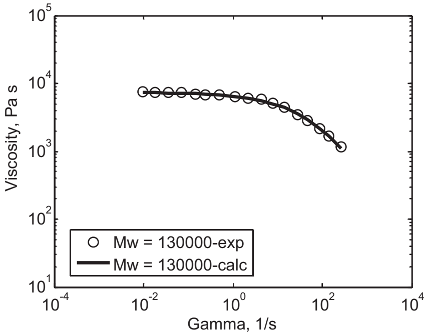

Figure 6.
Published [21] and calculated viscosity values at 200 °C

comprises the following equations:

$$\frac{1}{P_e}\frac{\partial^2 I}{\partial X^2}+\frac{\partial M}{\partial X}-t_0 v_{R,I}=0\ ;\quad X=0,\ I_0-I=-\frac{1}{P_e}\frac{\partial I}{\partial X}\ ;\quad X=1,\ \frac{\partial I}{\partial X}=0 \tag{2}$$

$$\frac{1}{P_e}\frac{\partial^2 M}{\partial X^2}+\frac{\partial M}{\partial X}-t_0 v_{R,M}=0\ ;\quad X=0,\ M_0-M=-\frac{1}{P_e}\frac{\partial M}{\partial X}\ ;\quad X=1,\ \frac{\partial M}{\partial X}=0 \tag{3}$$

$$\frac{1}{P_e}\frac{\partial^2 \lambda_m}{\partial X^2}+\frac{\partial \lambda_m}{\partial X}-t_0 v_{R,\lambda_m}=0,\quad m=0..2\ ;\ X=0,\ \lambda_m=-\frac{1}{P_e}\frac{\partial \lambda_m}{\partial X}\ ;\ X=1,\ \frac{\partial \lambda_m}{\partial X}=0 \tag{4}$$

$$\frac{1}{P_e}\frac{\partial^2 \mu_m}{\partial X^2}+\frac{\partial \mu_m}{\partial X}-t_0 v_{R,\mu_m}=0,\quad m=0..2\ ;\ X=0,\ \mu_m=-\frac{1}{P_e}\frac{\partial \mu_m}{\partial X}\ ;\ X=1,\ \frac{\partial \mu_m}{\partial X}=0 \tag{5}$$

where: I, I_0– current and feed initiator concentration; M, M_0-current and feed monomer concentration; λ_m – the moments of active polymers concentrations distributions ($m=0..2$); μ_m – the moments of dead polymers concentrations distributions ($m=0..2$); X - dimensionless axial length; Pe – the Péclet parameter of the AD model;

Table 5.
AD model parameters for Ludovic simulated RTD

Extruder mass flow rate, [kg/h]	Screw speed, [rpm]	Pe values	Mean residence time, [min]
0.75	50	44.2	7.54
0.75	200	30.0	5.84
0.75	300	28.2	5.67
1.25	50	57.6	5.38
1.25	200	32.3	5.00
1.25	300	30.4	3.61
1.50	50	68.2	4.82
1.50	200	35.0	3.25

The number-average molecular weight of the polymer is calculated based on the distribution moments of 0th and 1st order, following the relation:

$$Mn=(MW)\frac{\mu_1+\lambda_1}{\mu_0+\lambda_0} \tag{6}$$

with MW – the monomer molecular weight;

The "consumption rates" involved in balance equations (2) - (5) are described by the expressions:

$$v_{R,C_I}=k_i IM \tag{7}$$

$$v_{R,M}=k_i IM+k_p M\lambda_0+k_{tm}M\lambda_0 \tag{8}$$

$$v_{R,\lambda_0}=-k_i IM \tag{9}$$

$$v_{R,\lambda_1}=-(k_i IM+k_p M\lambda_0+k_{tm}M(\lambda_0-\lambda_1)+k_{ts}S(\lambda_0-\lambda_1)) \tag{10}$$

$$v_{R,\lambda_2}=-(k_i IM+2k_p M\lambda_1+k_p M\lambda_0+k_{tm}M(\lambda_0-\lambda_2)+k_{ts}S(\lambda_0-\lambda_2)) \tag{11}$$

$$v_{R,\mu_0}=-(k_{tm}M\lambda_0+k_{ts}S\lambda_0) \tag{12}$$

$$v_{R,\mu_1}=-(k_{tm}M\lambda_1+k_{ts}S\lambda_1) \tag{13}$$

$$v_{R,\mu_2}=-(k_{tm}M\lambda_2+k_{ts}S\lambda_2) \tag{14}$$

$$v_{R,C_S}=-k_{ts}S\lambda_0 \tag{15}$$

The mathematical model so defined was solved using a procedure based on the estimation function "bvp4c" (MATLAB).

Mathematical Modeling of PLA Reactive Extrusion Based on the Compartment Flow Model

As mentioned above, the regions with higher filling ratios (high degree of mixing) and higher residence time (kneading discs sections) are treated as perfectly mixed zones, whereas the transport sections, with low intensity of mixing and lower residence time, as plug-flow (smallest filling ratio) regions. The main elements for this simulation approach are presented in the Table 6 for the flow studies carried out by Ludovic® software. The data presented in this table are extracted by reading the local and global residence time profiles given by Ludovic® simulations in Figure 7.

Having the succession of ideal plug flow and perfectly mixed zones and the kinetic model, the calculation can be done successively, from the hopper to the die, starting with the known entry conditions.

The mass balance of the monomer for the ith perfectly mixed zone, assuming equal inlet and outlet volume flow-rates, has the form:

$$x^{i-1} = x^{i} - t_s^i v_{R,i} \qquad (15)$$

where x$_i$ represents the concentration of the species x in the ith region. From equations (15) one can successively calculate the concentrations and moments at the exit of the perfectly mixed region, by the Newton-Raphson method, knowing the feed concentrations and the mean residence times, t_s^i.The mass balance for the ith plug flow (PF) region is given by:

$$\frac{dx_i}{dt} = -v_{R,i}, \quad t = \frac{z}{u_{z,i}} \qquad (17)$$

where: x$_i$ - the concentration of the species x in the ith zone; $u_{z,i}$ - the flow speed in the ith zone; $v_{R,i}$ - the consumption rate of the x$_i$ species;

The integration of the PF model was performed by a procedure based on a fifth order Runge-Kutta algorithm implemented in MATLAB® programming package.

Reactive Extrusion Simulation Results

The L-lactide polymerization process occurring in the experimental extruder was simulated by the two mathematical models described above, based on the axial dispersion flow model and the compartment flow model respectively. A comparison of both modeling approaches for a flow rate of 0.75 kg/h and a screw speed of 50 rpm is given in Figure 8, as computed profiles along the screw axis. Further comparisons of the monomer conversion and number average molecular weight values calculated at the extruder exit by the two approaches are also presented in Table 7 for several operating conditions. As observed from Figure 8 and Table 7, no significant differences occur in predicting monomer conversions and number-average molecular weights by the two modeling approaches. It can be concluded that the two models predict practically the same results at the extruder exit, for both monomer conversion and number-average molecular weights, with slightly lower

Table 6.
The parameters for 1.25 kg/h, 50 rpm

Zone #	Type	Residence time,[s]	Zone length, [mm]
Zone 1	Plug-flow	27	300
Zone 2	Perfectly mixed	73	–
Zone 3	Plug-flow	35	300
Zone 4	Perfectly mixed	46	–
Zone 5	Plug-flow	14	177
Zone 6	Perfectly mixed	28	–
Zone 7	Plug-flow	20	223
Zone 8	Perfectly mixed	100	–
Zone 9	Plug-flow	2	50

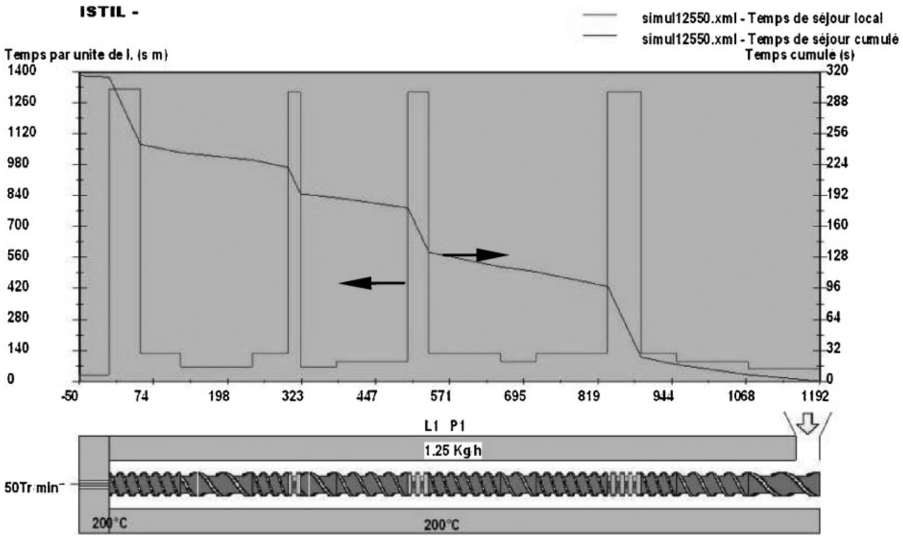

Figure 7.
Local residence times (s m^{-1}) and cumulated RTD curve (s), computed by Ludovic for 1.25 kg/h and 50 rpm. The abscissa of the diagram represents the position along the screw (mm), starting from the die.

monomer conversions for the compartment model.

The comparison of calculated polymer characteristics by the two mathematical models with the experimental data of the PLA reactive extrusion, presented also in Table 7, shows a reasonable accuracy of the model predictions for exit monomer conversion and number-average molecular weight. For the data given in this table, an average error of 4.7% occurs in the prediction of monomer conversion for the axial dispersion model and 9.9% for the compartment model. In the prediction of the average molecular weight, the mean errors are 12% for axial dispersion model and 10.7% for compartment model, respectively. These errors are in the acceptable range, taking into account the accuracy of the kinetic measurements and the approach

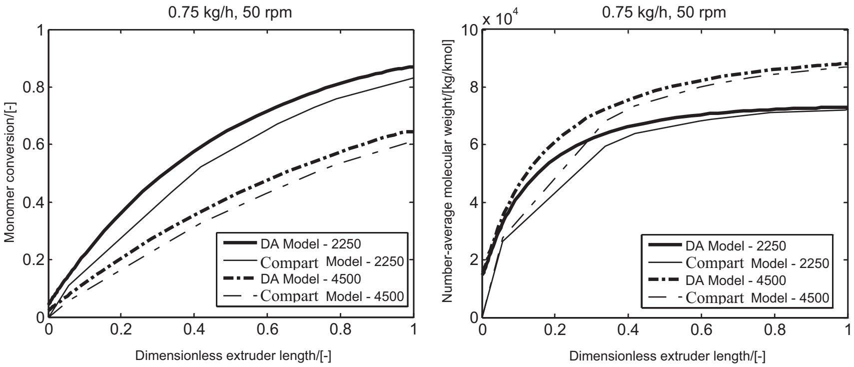

Figure 8.
Reactive extrusion simulation by the two modeling approaches (DA Model – axial dispersion model, Compart Model – Compartment model); the numbers in the legend represents the monomer to initiator (M/I) molecular ratio in the feed, with values of 2250 and 4500 respectively.

Table 7.
Experimental and predicted polymer characteristics for M/I = 2250

Mass flow rate, [kg/h]	Screw speed, [rpm]	Monomer conversion, [-]			Number-average molecular weight, [kg/kmol]		
		Exp	AD model	Compartment model	Exp	AD model	Compartment model
0.75	50	0.91	0.87	0.84	70000	73000	72500
0.75	200	0.82	0.80	0.74	63000	72000	71000
0.75	300	0.80	0.79	0.72	62000	71000	70000
1.25	50	0.87	0.78	0.75	65000	71500	71000
1.25	200	0.74	0.75	0.69	64000	71000	69000
1.25	300	0.68	0.63	0.58	60000	68000	67000
1.5	50	0.72	0.74	0.71	61000	71000	71000
1.5	200	0.65	0.60	0.55	59000	67000	66000

AD model: axial dispersion model

used in the description of flow and mixing of reaction mixture.

Among the two models used to describe the flow and mixing of reaction mixture, the axial dispersion model is more soundly formulated, its adequacy in this study confirming other works which recommend it for this type of flow systems.

The computed polydispersion index is below 2 for both models (1.8–1.9), while the experimental values are of the order of 2.4. Our model has to be improved, and as we will see in the conclusions, the main uncertainty lies in the kinetic model, which is one difficulty of this system.

Conclusions

This study presented a modeling approach for L-lactide ring-opening polymerization process by reactive extrusion. As a first step of the study, the kinetics of the L-lactide ring-opening polymerization initiated by $SnOct_2$/TPP was experimentally investigated; the results were used to develop a kinetic model of the process, predicting the monomer conversion and the average molecular weight of the polymer product. The model provides theoretical predictions in reasonable agreement with the experimental measurements.

In order to develop the mathematical model of the extrusion process, the flow and mixing characteristics of the reaction mixture were evaluated by using the simulation package Ludovic®. Based on the simulated RTD data for the L-lactide polymerization mixture in the TSE, the material flow and mixing were described by two flow models: (i) the axial dispersion model and (ii) a compartment model consisting in a series of ideal perfectly mixed and plug flow zones. By coupling these flow models with the polymerization kinetic model, two extrusion process models were built. These were used to predict the monomer conversion and number average molecular weight of the polymer. A reasonable good agreement between the calculated values and experimental data were obtained, this confirming the validity of the modeling approach. These results are also confirming that the axial dispersion model is a valuable tool for modeling the reactive extrusion processes.

The accuracy of the modeling results could be improved by using a more rigorous kinetic model, including the reversibility of the polymerization process, the influence of the impurities present in the reaction mixture as well as the description of the polymer molecular weights distributions (polydispersion index). Further improvement of the process model is also possible by including more accurate data concerning the L-lactide/PLA melt flow in the twin-screw extruder.

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