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Microwave energy assisted synthesis of poly lactic acid *via* continuous reactive extrusion: modelling of reaction kinetics

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The most commonly used batch process to manufacture PLA is ring opening polymerization (ROP) of lactide monomer in a suitable solvent, in the presence of a metallic/bimetallic catalyst (Sn, Zn, and Al) or other organic catalysts. However, this process does not lend itself to safer/cleaner and high throughput (and high volume) manufacturing. Continuous reactive extrusion of lactide monomer using a suitable reaction input has the potential to increase the throughput, and this route has been explored in the literature. In this work, reactive extrusion experiments using stannous octoate $Sn(Oct)_2$ and tri-phenyl phosphine $(PPh)_3$, were considered to perform ROP of lactide monomer using the microwave as an alternative energy (AE) source for activating and/or boosting the polymerization. Implementation of a microwave generator in a section of the extruder is one of the novelties of this research. A simulation model of ROP of PLA was formulated to estimate the impact of reaction kinetics and AE source on the polymerization process. Ludovic® software was used for the simulation of continuous reactive extrusion of the process. Experimental and simulated results were compared for the validation of the methodology. This work also highlights the advantages and drawbacks of most conventional metal catalysts, the effect of alternative energies on reaction mechanism, and safe and efficient production of PLA.

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1. Introduction

The production of waste, especially from consumable products, is one of the major challenges of the present era. Polymers represent 20–30% of global waste,[1,2] leading to problems such as decomposition and recycling of the polymers. As alternatives, bio-mass and/or bio-degradable polymers such as cellulose acetate (CA), poly-butylene succinate (PBS), poly-lactic acid (PLA), poly-urethane (PU) *etc.* have gained interest. Among these bio-plastics, poly-lactide or poly lactic acid (PLA) has been gaining interest in the past few decades.[2–5]

For decades, the conventional commercial method for synthesis of PLA was ring-opening polymerisation (ROP) based on metal (Sn, Al, Zn) catalysis of lactide using suitable co-catalyst such as dodecanol in a suitable solvent (toluene).[1,6–11] However, PLA produced using the conventional methods may contain traces of the metal catalysts, restricting the potential applications for the final product.[6]

Several attempts were made to substitute tin-based catalysts by catalysts that exhibit less toxicity or eco-toxicity.[8–16] Typically, the alternative catalysts require a higher amount of energy of activation.[17] Initial experimental trials support the use of alternative energy sources (LASER, Ultrasounds, microwaves) to facilitate the ROP of lactide monomers.[18–27]

Several projects and research groups are trying to optimize the polymerization of PLA through cleaner, efficient and safer processes.[15,26–28] One such project is InnoREX.[28] The main aim of this project was to combine eco-friendly catalysis with reactive extrusion (REX) for ROP of lactide to obtain a high throughput.[29,30,32] The project also explored the use of alternative energy sources (microwave, ultrasound) to reduce the total energy consumption and further increase the eco-friendly credentials. Application of microwave heating to chemical reactions has received a lot of attention in the past few years.[15] Due to its qualities such as high efficiency, the capability of uniform heating and reduced reaction time, a large number of chemical reactions undergo a significant increase in reaction speed due to microwave irradiation compared to the general methods for heat-irradiation such as furnace chamber and LASER heating *etc.*[17–20] Liu *et al.*[19] and Cheng *et al.*[20] investigated the microwave-assisted radical polymerization of styrene with a faster polymerization rate in comparison to conventional heating. Some studies were also conducted to produce PLA. The first microwave-irradiated polymerization of D,L-lactide to

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support the reaction process for higher output was reported by Albert *et al.* and Liu *et al.* AE source was used as source of heating to provide a suitable energy for polymerization process.[18,19,33]

Based on several reactive extrusion experiments results from Dubey *et al.*, Banu *et al.*[29,30,34,35] concluded that the combination of microwave heating technology and living free radical polymerization (LRP), can increase the rate and effectiveness of reactions.[25] It must, however, be added that although there are studies that use AE in reactive extrusion, to the best of the author's knowledge, there is there is no comprehensive study in the area of modelling ROP of lactide process mechanism when AE in the form of microwave energy is used.

In this work, the impact of AE on ROP of LA using metal catalyst was investigated through reactive extrusion experiments and validated by modelling the reactive extrusion using Ludovic® software.[32] The reported study can be divided into three different stages Fig. 1. (1) Extrusion experiments – to obtain experimental data of ROP of LA using stannous octoate ($Sn(Oct)_2$) as catalyst and applying microwave; (2) simulation of batch process, using initial parameters of extrusion experiment (Dubey *et al.*[29,30]), to obtain isothermal curves; and (3) implementation of the isothermal curves (output of step 2) in Ludovic® software[32] to simulate reactive extrusion process of PLA formation.

2. Materials and processes

2.1. Materials details

The monomer used for the reactive extrusion was L-lactide (Sigma-Aldrich), the catalyst, co-catalyst and initiator were stannous octoate ($Sn(Oct)_2$) (Sn-bis(2-ethylhexanoate), Sigma-Aldrich), triphenylphosphine $(PPh)_3$ (Sigma-Aldrich), and 1-dodecanol (Sigma-Aldrich), respectively.

2.1.1. Experimental process: reactive extrusion of PLA. Reactive extrusion experiments were performed at Fraunhofer, ICT laboratory,[31] using Leistritz 27 HP, a co-rotating twin screw extruder. The configuration of the twin screw extruder are as follows: 18 mm diameter barrel and length/diameter ratio (L/D) = 52, temperature range (160–200) °C. Microwave energy was applied in this process using a 'Microwave Device' (MUEGGE, Germany[26]) for 3–15 minutes. Microwave source range (0.5 GHz min to 5.8 GHz max) was implemented. For this particular research work industrially relevant frequencies of 2.45 GHz were implemented for heating the material in the reaction process. An extruder window block was specifically designed to facilitate the application of microwave. Based on several trials for microwave device position, the device was mounted in this block at a distance of 25 D from the feeding zone. See Fig. 2.

Fig. 2 Microwave incorporation block to the twin-screw extruder MUEGGE®.

For the reaction, monomer and catalysts were pre-mixed under inert gas atmosphere to avoid moisture impurities and fed into main feed. The initial concentration of the reactants and some initial conditions of the experiments are shown in Table 1.

2.2. Characterisation techniques

Monomer conversion (X) and average molecular weight ($\overline{M_n}$) were measured at several temperatures, time and molecular monomer to initiator ratios. Then, samples were taken at different stages of the reaction process to evaluate the polymerization efficiency.

2.2.1. Gel permeation chromatography (GPC). Gel Permeation Chromatography (GPC) device [Polymer Standards Service GmbH (PSS), USA] was equipped as follows:

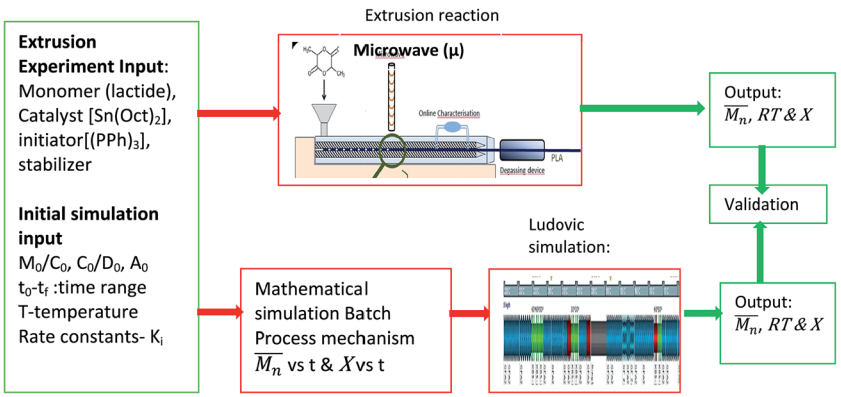

Fig. 1 Schematic to explain reaction parameters. M_0: initial concentration of monomer, C_0: initial concentration of catalyst $Sn(Oct)_2$, D_0: initial concentration of OH group source, A_0: initial concentration of octanoic acid (OctOH), ($\overline{M_n}$) number average molecular weight, X: conversion, RT: residential time, K_i: rate constants.

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Table 1 Twin-screw extrusion reaction parameters

Symbol	Parameter	Value (unit)
M_0	Initial concentration of monomer	8.3 mol L^{-1}
C_0	Initial concentration of catalyst	0.008 mol L^{-1}
D_0	Initial concentration of co-catalyst	0.008 mol L^{-1}
T_0	Initial feeding temperature	30 °C
M	Monomer mass flow	0.5–2.0 m kg^{-1}
rpm	Rotational speed	40 to 1000 rpm

Table 2 Initial reaction parameters for simulation

Symbol	Parameter	Value (unit)
M_0	Initial concentration of monomer	8.326 mol L^{-1}
C_0	Initial concentration of catalyst	0.008 mol L^{-1}
D_0	Initial concentration of co-catalyst	0.008 mol L^{-1}
T_0	Initial temperature	30 °C
A_0	Octanoic acid (OctOH)	0.24 mol L^{-1}
M_e	Monomer equilibrium concentration	0.225 mol L^{-1}

• Poly(styrene sulfonate) (PSS) (series 1100, Agilent), at 35 °C;
• Columns: [PSS PFG 7 μm 8 × 50 mm (guard column) PSS PFG 7 μm 8 × 300 mm; 100 A PSS PFG 7 μm 8 × 300 mm; 1000 A];
• Flow: 1, 0 mL min^{-1};
• Refractive Index Detector Agilent 1100;
• Injection volume: 100 μL;
• Hexafluoroisopropanol (HFIP) as a solvent;

Calibration was based on solutions of poly-(methylmethacrylate) (PMMA), the values were not absolute, but relative to the standard used.

2.2.2. Proton nuclear magnetic resonance (^{1}H-NMR). Proton nuclear magnetic resonance analysis was conducted in $CDCl_3$ using a Bruker (250) MHz spectrometer (Coventry, UK) at 30 °C. The solution concentration used was 5 w/v%. This technique was applied to determine the monomer concentration and from that the conversion rate (X). This analysis was also applied to the sample collected from the extruder, which was a mixture of monomer and polymer. Several numbers of scans (100) were performed for each sample.

3. Mathematical modelling of reactive extrusion

Developing the simulation model which defines the extrusion process was divided into two parts: firstly the development of a mathematical model describing the rate kinetics of ROP reaction in the batch process, and secondly integrating this model into Ludovic® software. From the ROP model for the batch process, isothermal curves for the evolution of number average molecular weight ($\overline{M_n}$) and conversion (X) with time were obtained. These curves were discretised and integrated (table input) in Ludovic®. This way, Ludovic® was developed and described in detail by Dubey *et al.*[33]

3.1. Reaction kinetics modelling and mathematical simulation of ROP of lactide

The reaction mechanisms of ROP of PLA were studied and the mathematical modelling using $Sn(Oct)_2$ as catalyst was developed and described in detail was reported by Dubey *et al.*[29,30] The model covered the details of mathematical modelling of polymerization of lactide, based on five stages of the reaction mechanism, that is initiation, propagation, termination (intermolecular mainly), *trans*-esterification and non-radical random chain scission.

The kinetic parameters involved in the reaction mechanism such as several rate constants (k values) k_p, k_d and monomer at the equilibrium concentration ($M_e = k_p/k_d$) *etc.* were taken straight from the literature.[30] Dubey *et al.*[29,30,33] covers mostly the details of research work related to mathematical modelling of ROP process of lactide in last 10 years or so. This mathematical model provided the isothermal curves that were implemented in Ludovic®. For the generation of the isothermal curves, the initial reaction inputs (Table 2) were selected according to the experiments on reactive extrusion conducted by Fraunhofer ICT.

The isothermal curves, conversion (X) and number average molecular weight ($\overline{M_n}$) with time, for the total reaction time of 30 min (0.50 h) and temperature range of (160–230) °C were

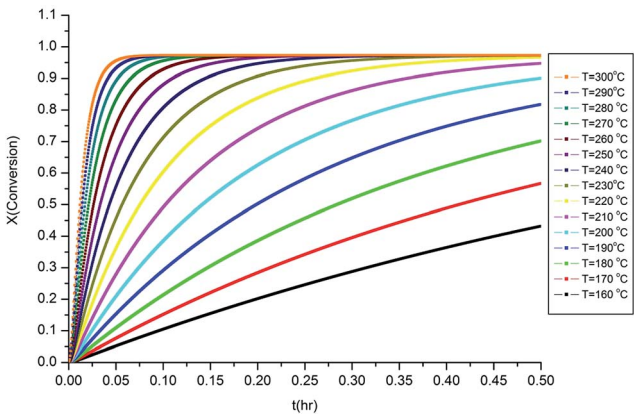

Fig. 3 Isothermal curves for conversion (X) *vs.* t.

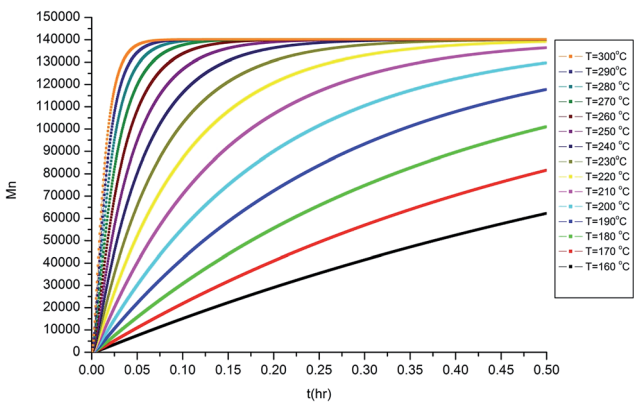

Fig. 4 Isothermal curves for average molecular weight ($\overline{M_n}$) *vs.* t.

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developed to facilitate input for Ludovic®. The duration of the input data was based on the residence time reported by experiments on reactive extrusion of PLA. Details of the input data are shown in Fig. 3 and 4.

3.2. Modelling of ROP reaction mechanism in reactive extrusion

Ludovic® is one of the most used software's for the simulation of extrusion processes.[31–33] At present, commercial versions of this software do not come with an option to simulate reactive extrusion, *i.e.* when a reaction happens during the extrusion process (within the extruder barrel). In order to adapt the software for accurate simulation of ROP of PLA, it was necessary to introduce the effect of the reactions happening within the extruder barrel on the properties of the system *i.e.* variation of the concentrations of initiator, monomer, polymer and their varying percentages as the reaction progresses, variation of parameters like temperature, pressure, *etc.*

Ludovic® software works by breaking down the extrusion process (along the barrel) into small subsections (nodes). Then, Ludovic® performs an iterative process (this is explained in the next section) to calculate all the parameters from the die to the hopper. With the implementation of the isothermal curves (molecular weight *vs.* time, viscosity *vs.* time, shear rate *vs.* time, *etc.*) it is possible to use Ludovic® to estimate the effect of the reaction into the extrusion parameters and to predict the outcome over each of the subsections. Details regarding the parameters and modelling method are well defined in one of our previously published work.[30]

A flowchart about the development of the whole simulation process is presented in Fig. 5.

3.2.1. Mechanism of reactive extrusion through Ludovic®. Simulation through Ludovic® detailed the thermo-mechanical behaviour of twin screw extruders.[32] 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. Stationary thermo-mechanical flow is computed on the basis of:

Geometrical discretization of the channel zone-C chamber of the screw and material flow of the mixture, as shown in Fig. 6.

Changes in pressure and temperature are computed for discrete volumes. Temperature and pressure both updated from the exit to the upstream part of the screw.

For the sensitivity of temperature effect, Ludovic® provides the temperature at each C-chamber zone Fig. 6. This temperature is the result of mechanical friction, conduction and alternative energy applied within the extruder. The geometry of the extruder, rotation speed of the screw, throughput and melt influence are factors that affect the mechanical energy from shearing; and this impacts the thermal response of the material.

3.2.2. Alternative energy implementation in Ludovic® software. In literature, to the best of the authors' knowledge, application of AE source within Ludovic to obtain the simulation of continuous reactive extrusion has not been reported. The basic principle behind considering AE source in the reaction process is as the source of heat or thermal impact on reaction mechanism. Due to its unique application, the effect of AE source on reaction is different to those that occur during conventional heating (Heat Furnace). AE source device was installed to the barrel lane (Grey Zone) in Ludovic® Fig. 6. The two specific requirements are

- Hollow cylinder zone (no metal screw, kneading *etc.*)
- Fully filled zone

To make the application of AE source (microwave) effective, full filled zone is to be designed under the alternative energy input section. Fig. 6 (ref. 32) shows an example of screw configuration setup with AE source barrel (chamber in grey colour).

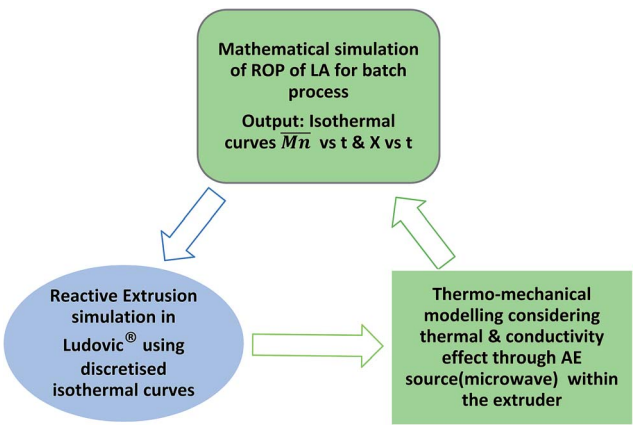

Fig. 5 Input and output for continuous extrusion simulation.

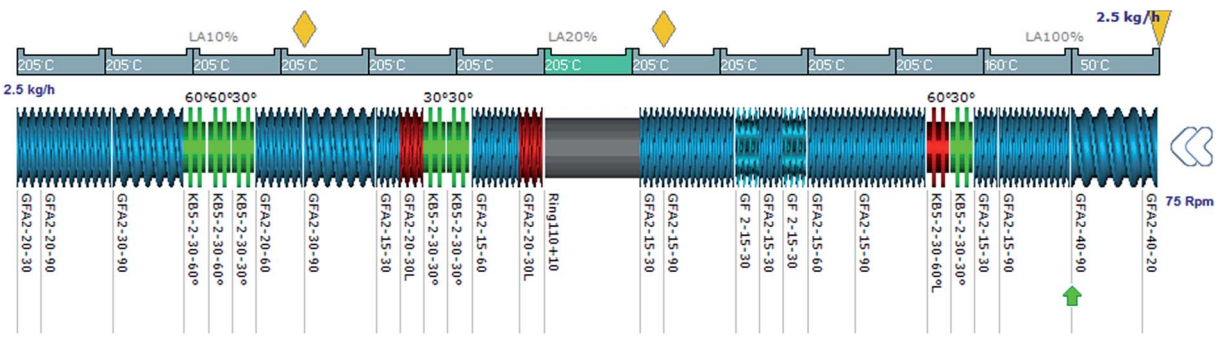

Fig. 6 Screw profile with AE source device.[32]

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3.2.3. Thermo-mechanical modelling of Ludovic. Consideration of two crucial physical parameters, conductivity and mechanical dissipation, for the thermal balance equation was made. The equation has AE source power as a third term under AE source (microwave) barrel. The updated heat equation is:

$$\rho \times C_p \times dT/dt = W_{dissipation} + W_{conduction(screw)} + W_{AE(microwave)} \quad (1)$$

This equation is then computed in each element and Ludovic® provides the variation of temperature due to AE source (Fig. 7) with the associated effects of thermal and conduction. Finally, these three effects are combined in order to finalise the global evolution of temperature within the twin screw extruder.[32]

Fig. 7 shows the contribution of 3 different effects to the variation of temperature. The feeding zone is at the right corner and the mixture flows from right to left side. In fact, in AE source zone, no barrel regulation is mounted also due to the use of the ring (no screw), the shear effect is negligible and only AE act as the source of heating.

For the application of the alternative energy in the reaction process, microwave source or Ultrasound Sonification seems to impact the polymerisation reaction system.[17–24] The AE power impact is taken into account as a third term (in addition to conduction and dissipation power) in the thermal balance equation.[1]

4. Results & discussion

4.1. Experimental result

Data of average residence time (RT), temperature (T), the number average molecular weight ($\overline{M_n}$), average molecular weight ($\overline{M_w}$) and conversion (X) from the reactive extrusion experiments using microwave during reaction process are provided in Table 3. It was observed that increase in temperature results in an increase in $\overline{M_n}$, $\overline{M_w}$ and X for the same initial conditions. Also, $\overline{M_n}$, $\overline{M_w}$ and X increase when microwave (AE) source is applied. For example, in the experiment at 180 °C, the value of conversion was found to be higher (80%) when the microwave was applied than in the case without the microwave (62%). A similar trend of increase in conversion (X) was also observed at 160 °C.

4.1.1. Impact of AE source on extrusion experiment. Microwave energy can influence different stages of the reaction system depending on the position where it is introduced into the

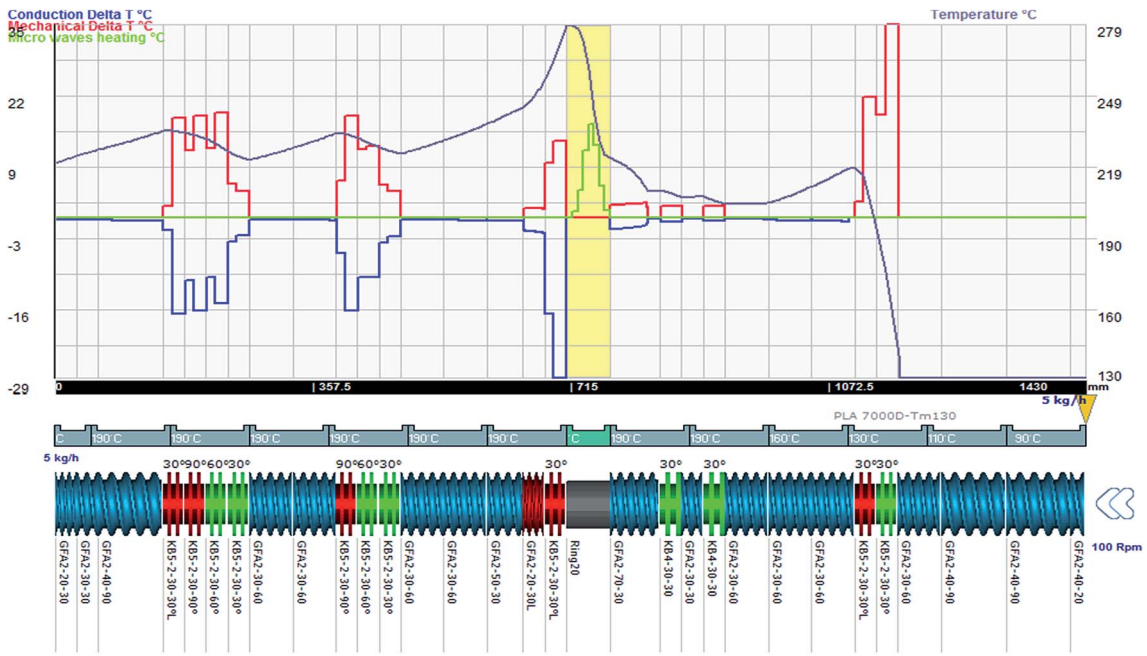

Fig. 7 Temperature variation due to conduction (purple), due to mechanical effect (red) and micro-wave (AE) (100–300 W) (green) effect and result on final temperature (grey).

Table 3 Reactive extrusion experimental data

RT (min)	T (°C)	Microwave	$\overline{M_n}$ (g mol^{-1})	$\overline{M_w}$ (g mol^{-1})	rpm	X (%)
20	180	Yes	34 763	50 059	600	80
		No	31 456	44 256	600	62
16	160	Yes	38 681	57 636	300	85
		No	33 564	50 653	300	70

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system. Different effects can be obtained: from mainly preheating the material, when introduced at a too early stage, to efficient heating of a main lactide containing reaction mixture, through to temperature homogenisation and local overheating when placed at very late extrusion stages. When using a matching combination of microwave incorporation position and underlying screw configuration, impressive influence, roughly M_n (39 000) g mol^{-1} on the reaction can be noted.

The application of microwave energy directly to the polymerisation mixture allowed the temperature to be increased quickly and efficiently, resulting in improved lactide conversion and molecular properties. However, when introduced at high temperatures or at a late reaction stage, the addition of microwave energy can increase the overall temperature excessively that causes backbiting reaction to dominate and resulting in polymer degradation.

4.2. Results of reactive extrusion simulation (Ludovic®)

4.2.1. Extrusion simulation without AE source. The simulation of the extrusion process has been performed by taking in account the absence and presence of AE source in the reaction process.

The area of μ-wave is designed in order to test the effect of such alternative energy Fig. 8. In this section, only results without μ wave are presented.

Fig. 9 shows the screw design and the evolution of temperature and residence time and the evolution of the kinetics. This kinetics has been introduced within Ludovic with the model presented in Fig. 2 and 3 of our previous work.[30] Similarly, Fig. 10 shows the variation of M_n and X with time and temperature.

4.2.2. Extrusion simulation with AE source. In order to be able to install the microwave equipment, a similar screw design than the previous one (see Fig. 6), has been designed (the only difference consists in the element after the hollow part replaced by a reverse element in order to ensure a totally filled hollow elements).

In such configuration and for standard operating conditions (300 rpm, 1 kg h^{-1}), on Fig. 11, the evolution of temperature and residence time are illustrated. The level of power is 250 W. It is noticed that the evolution of temperature in the area of microwave equipment is important but finally it does not exceed 200 °C. The final residence time stays for 430 seconds until the final mixing zone which seems to be useless. On Fig. 12, the evolution of conversion ratio (X) and molecular

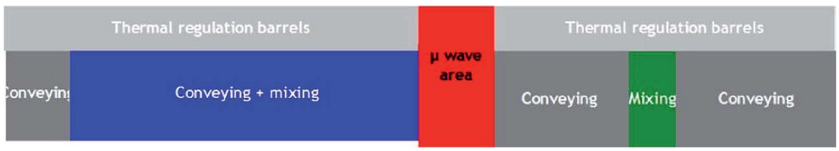

Fig. 8 Screw design and material mixing-Leistritz 18 mm screw diameter.

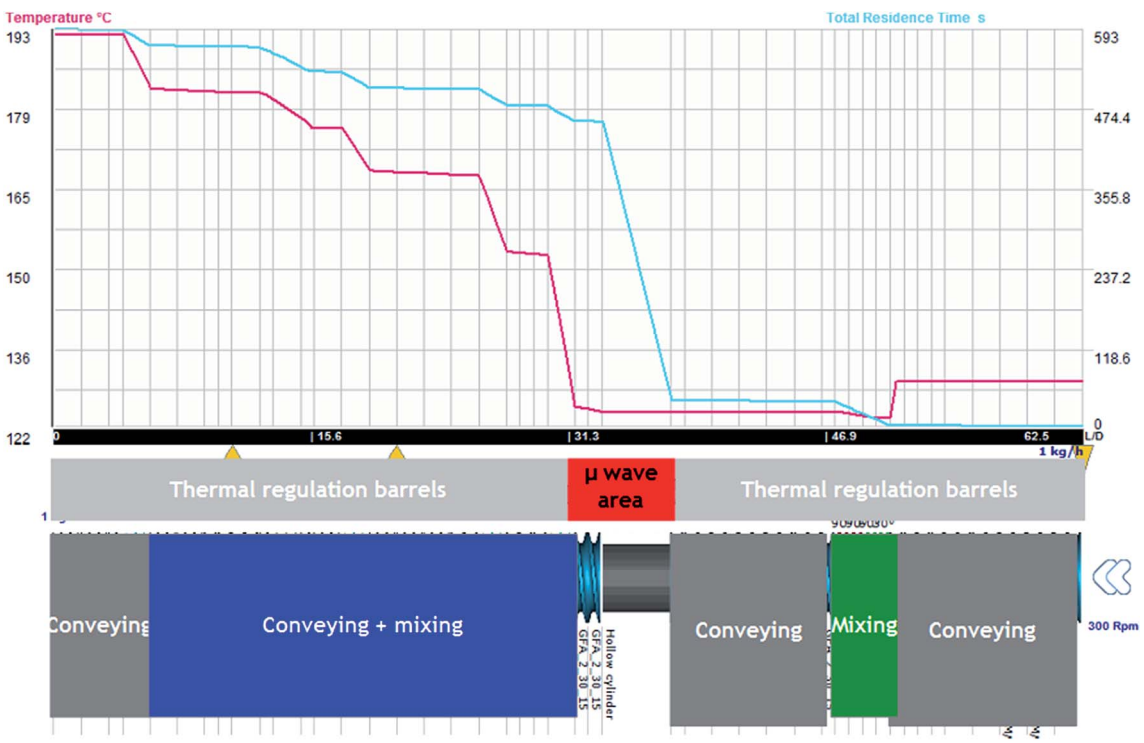

Fig. 9 Evolution of temperature (red) and residence time (blue) in extruder.

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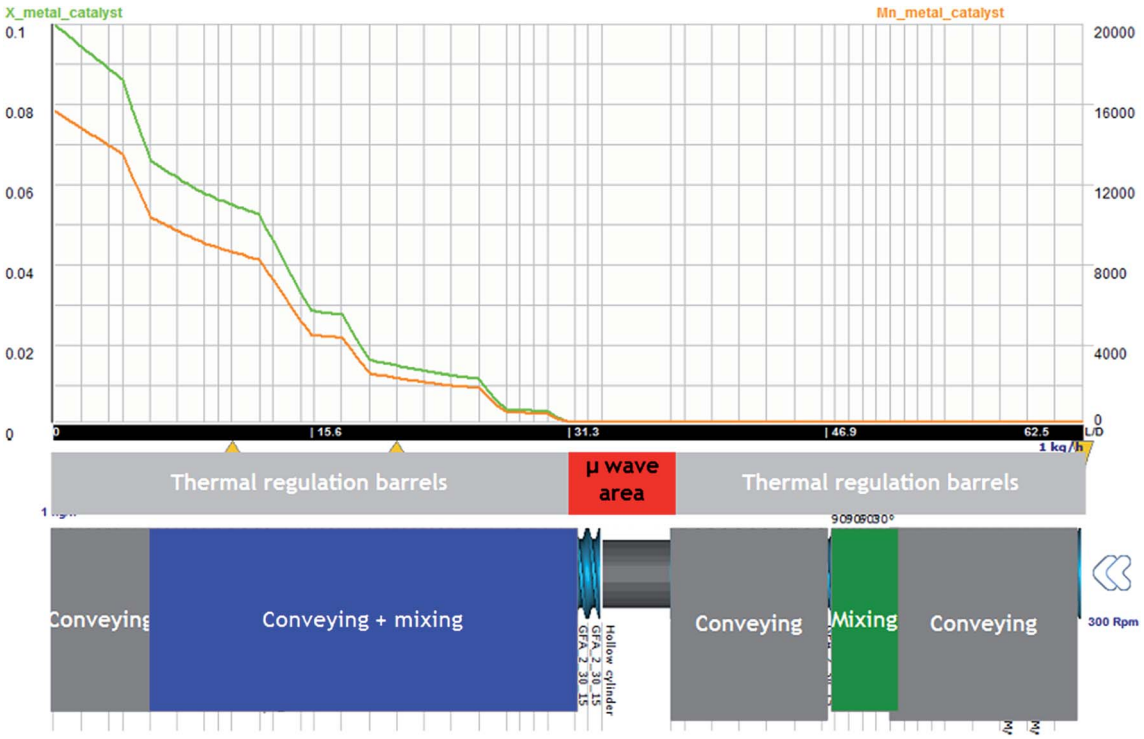

Fig. 10 Evolution of conversion ratio (green) and molecular weight (orange) in extruder.

weight (M_n), confirm the interest of such equipment which speeds up the reaction.

This analysis is necessary to keep in mind for the support of the scaling up design for the industrial case.

The impact of AE source shows very clear in (Fig. 11 and 12) that microwave energy boost the variation in temperature of the reaction process and total residence time. Similarly, the impact of AE source influences the variation in X and M_n. So the

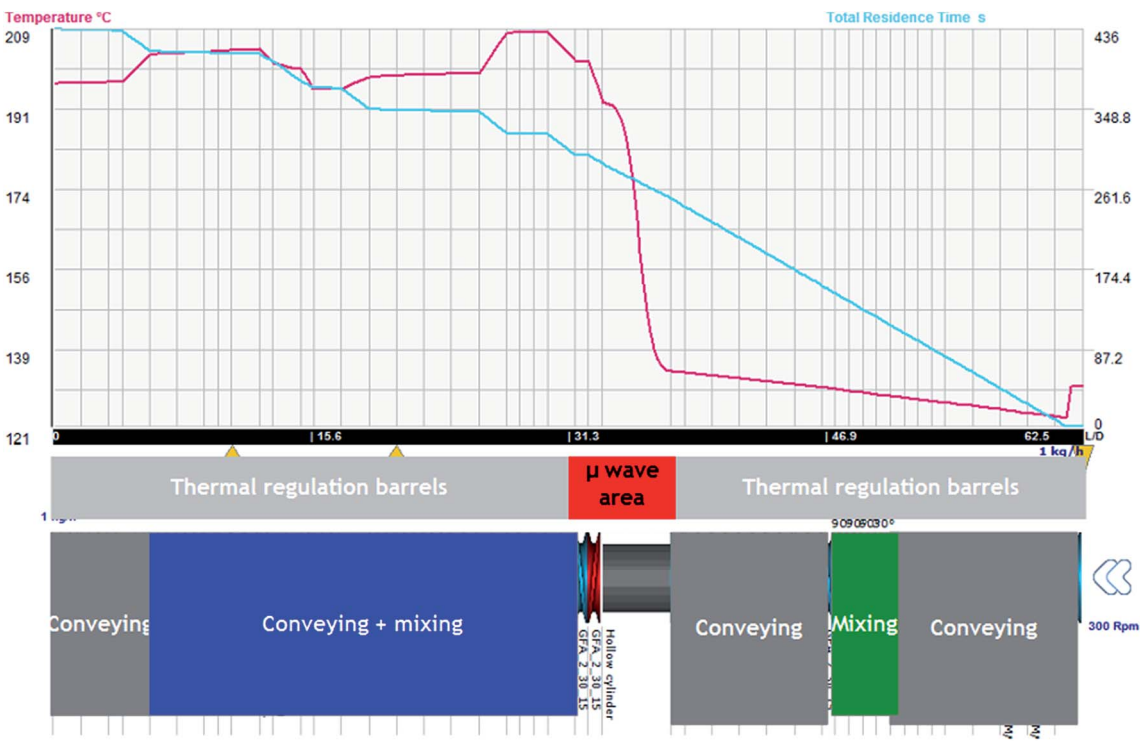

Fig. 11 Evolution of temperature (red) and residence time (blue).

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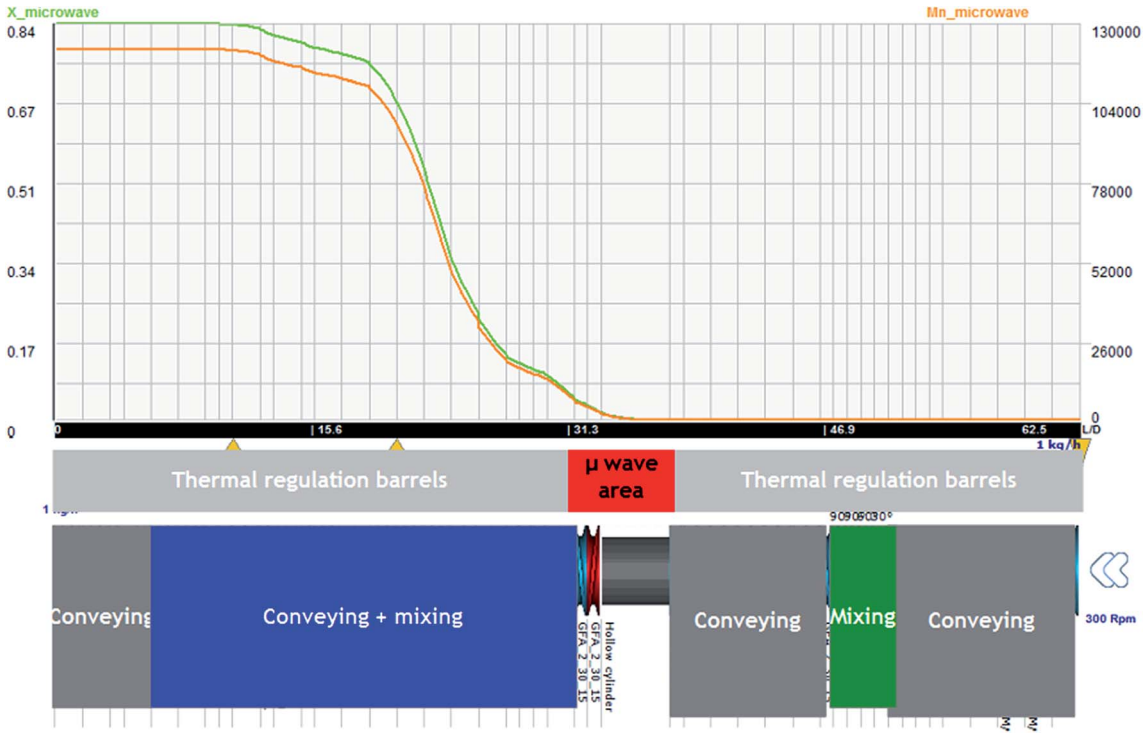

Fig. 12 $\overline{M_n}$ (orange) *vs.* *T* & *X* (green) *vs.* *T* obtained with Ludovic® for *T* (50–220) °C, AE = 250 W, 300 rpm.

positive impact of AE source in the extrusion process both in experimental and simulation modelling process has been easily shown.

4.2.3. Comparison of extrusion experiment and Ludovic® simulation results

(a). RTD comparison with throughput and barrel temperature. The performed correlations regarding residence time distribution (RTD) through residual lactide (RL) with rpm and barrel temperature are presented in Fig. 13. For Ludovic, the residual percentage of lactide (% LA) is represented by 1-conversion ratio. Through comparison, it was found that the residual % LA is not representative of the evolution of kinetics as the function of time and temperature. For Ludovic simulation, the barrel temperature shows the very limited effect on residence time and temperature. Potentially, this is the reason why the conversion ratio is not sensitive. For extrusion experiment and simulation, the variation of RL seems to be very different in general.

4.3. Average molecular weight comparison at various temperatures

Simulation and experimental extrusion process results for the average molecular weight (M_n) at various temperature shows that, at low temperatures, the M_n value reported through Ludovic® is higher than that for the experiment. This is related to the higher residual lactide (RL) reported through Ludovic® than the experiment (Fig. 13). If RL is high signifies, RT is high, it means the material mixture remains for a long time in the mixing chambers which facilitates the proper polymerization process and produces the high output. Proper mixing of material in the extruder chamber is one of the key features for

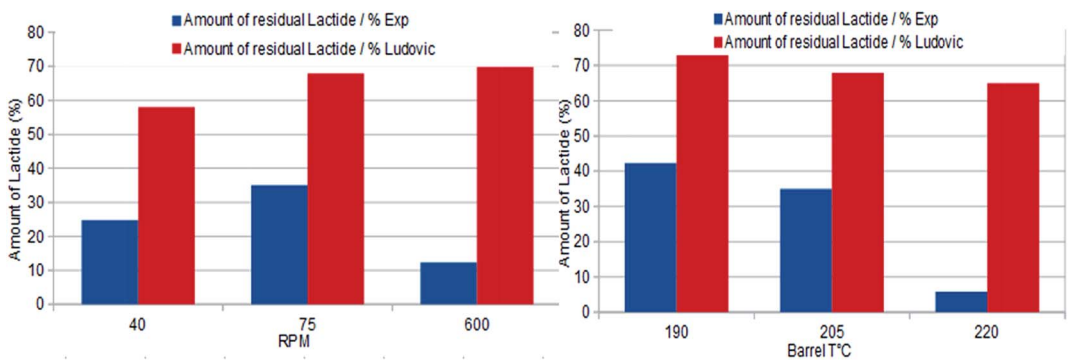

Fig. 13 Correlation of residual lactide according to rpm & correlation of residual lactide according to barrel temperature.

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Table 4 Comparison between simulation ("Ludovic®") and experimental results ("Expt.")

S. no.	Temp. (°C)	$\overline{M_n}$ (Expt.) (g mol^{-1})	$\overline{M_n}$ (Ludovic®) (g mol^{-1})
1	160	38 681	40 580
2	180	34 763	36 456
3	200	32 102	34 011

optimum polymerization. As temperature increases, M_n starts falling down. This can be explained by the activation of side reactions at a thermal threshold, as a result of the heat contribution of the AE source. The values of M_n through extrusion experiment and Ludovic® has been mentioned in Table 4.

5. Conclusions

Reactive extrusion of PLA aided by AE (microwave) source was successfully conducted at Fraunhofer ICT lab and based on initial reaction data. Simulation of reaction mechanism has been conducted to further provide input for modified Ludovic® software and validate both experimental and simulation outputs. This implementation poses a step forward in the state-of-the-art of ROP of lactide both technically and analytically. The use of AE source has a positive impact on the reaction process as reported above both experimentally and through theoretical simulation. The application of the AE source shows the boost in RT and in the result, higher M_n values. In general microwave energy, as a source of heat facilitated the polymerization process up to a certain temperature range (160–180) °C. At higher temperatures, the effect of the microwaves was observed not very promising as it can trigger side reactions that degrade the PLA chain. The implementation of AE sources (microwave or ultrasound) for PLA production can be chosen based on the experimental setup (temperature range) and application. Overall, the impact of AE source is proven to be positive for the reactive extrusion process for PLA formation. Further investigation will be made based on new experimental trials considering the more wide range of temperature and the new class of eco-friendly catalyst and co-catalyst combinations.

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