Attachment holding figures and tables to Final Report Summary – InnoREX

Project logo

Partner	Role within Project/ Competences	Contact
Fraunhofer ICT	Coordination of the project Online analytics: NIR Combining all elements to InnoREX production line Process realisation	Björn Bergmann Phone +49 721 4640-423 bjoern.bergmann@ict.fraunhofer.de
Gneuss GmbH	Online viscometry MRS degassing extruder Filtration Systems Measurement technology	Alexander Frank Phone + 49 5731 5307 122 alexander.frank@gneuss.de
University of Mons	Catalyst development Reaction kinetics	Jean-Marie Raquez Phone +32 65 37 34 81 jean-marie.raquez@umons.ac.be
Hielscher Ultrasonics GmbH	Ultrasound incorporation	Thomas Hielscher Phone +49 33 28 43 73 thomas@hielscher.com
Muegge GmbH	Microwave incorporation	Joachim Schneider Phone +49 6164-9307-66 joachim.schneider@muegge.de
Sciences & Computers Consultants Sarl	Enhancing Ludovic software	Chantal David Phone +33 4 77 49 75 82 scc@scconsultants.com
Materia Nova	Life Cycle Analysis	Olivier Talon Phone +32 65 55 49 18 olivier.talon@materianova.be
BH Industries	Upscaling strategy	Marian Soja Phone +48 69 39 31417 m.soja@bhiproject.pl
Talleres Pohuer SL	Injection moulding	Pablo Querol Phone +34 96 555 09 35 investigacion@pohuer.es
Asociacion de investigacion de materiales plasticos y conexas – AIMPLAS	Additivation strategy Sheet extrusion	Carolina Losada Phone +34 961 366 040 closada@aimplas.es
Associazione nazionale costruttori di macchine e stampi per materie plastiche e gomma - ASSOCOMAPLAST	Dissemination and Exploitation	Girolamo Dagostino Phone +39 028 228 37 54 g.dagostino@assocomaplast.org
Cranfield University	Modelling of reaction kinetics in extrusion conditions	Hrushikesh Abhyankar Phone +44 1234758085 h.a.abhyankar@cranfield.ac.uk

List of beneficiaries and contact names

Description of the main S&T results / foregrounds

University of Mons: Catalyst development for the bulk polymerization of *L*-lactide

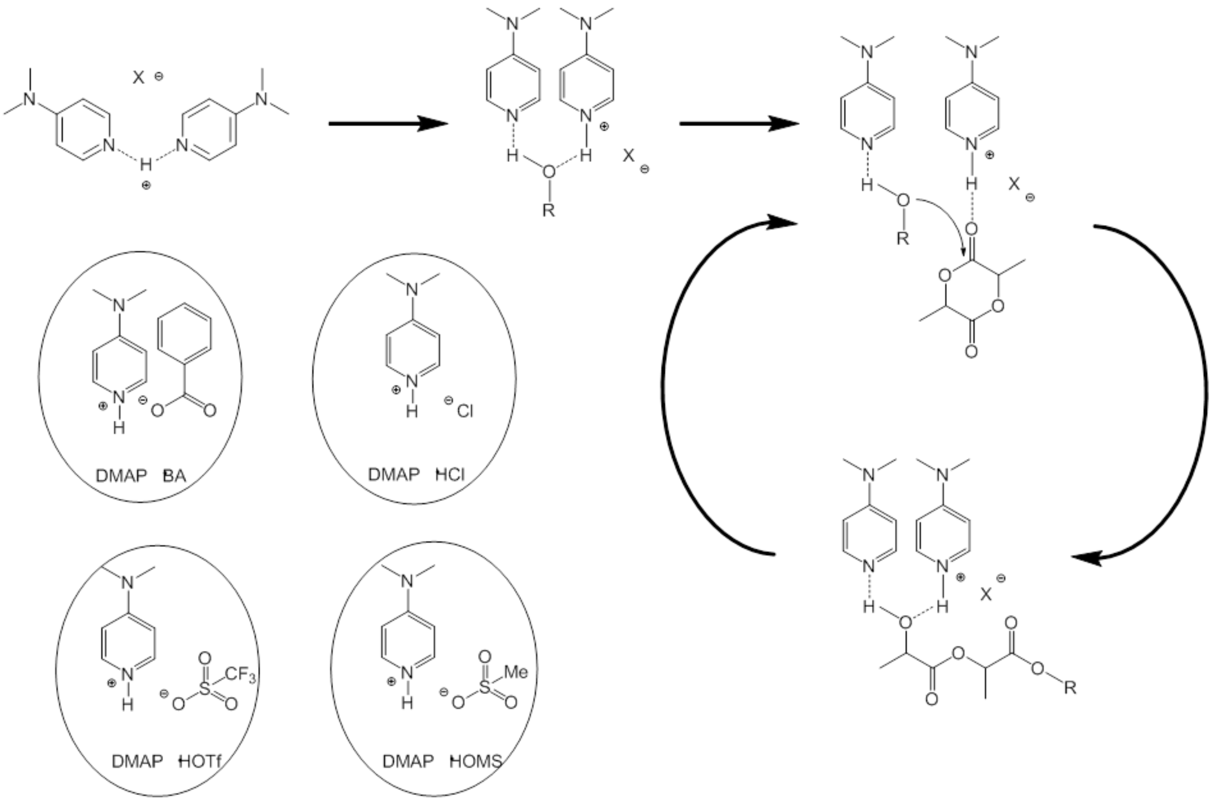


Figure 1: Proposed mechanism for DMAP/DMAP.HX catalysed ROP of lactide (X is benzoate, chloride, trifluromethane sulphonate, methane sulphonate)

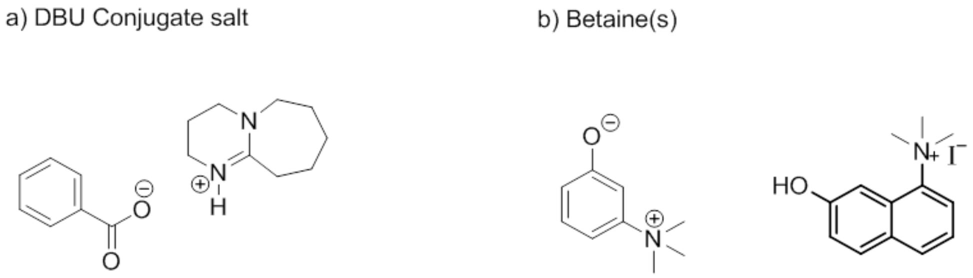


Figure 2: Examples of organic catalysts a) DBU benzoate conjugate salt and b) (trimethylammonio)-phenolate betaine and (7-Hydroxylate-naphthalen-2-yl)-trimethyl-ammonium

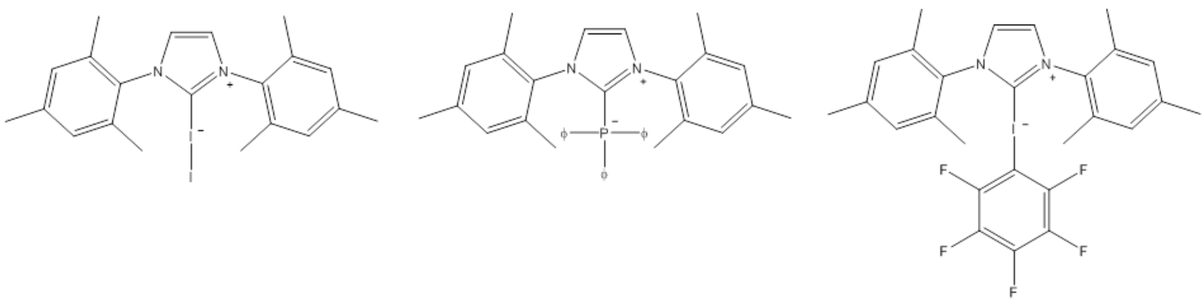


Figure 3: Examples of 5-membered carbene catalysts

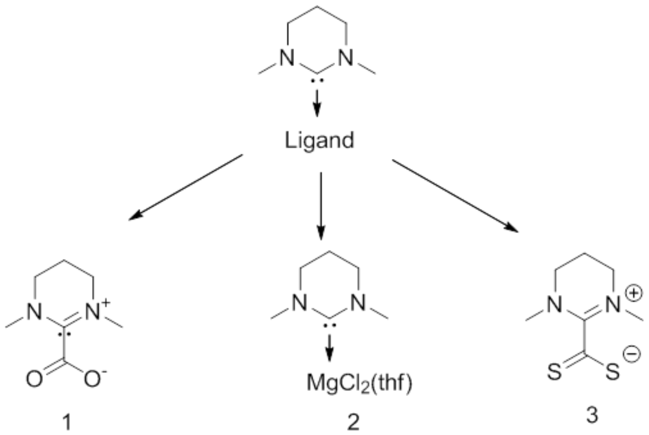


Figure 4: 6-membered N-heterocycle carbenes 1) 1,3-dimethyl-3,4,5,6-tetra- hydropyrimidin-1-ium-2-carboxylate 2) 1,3-dimethyl-3,4,5,6-tetrahydro pyrimidin-1-ium-2-MgCl2 (Mg-NHC) 3) 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-1-iu- m-2-carbodithioate

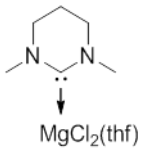


Figure 5: 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-1-ium-2-MgCl2 (Mg-NHC)

Table 1: Characterization data for P(L-LA) obtained by carbene-MgCl2 (six-membered ring NH) catalyst polymerization at 170°C& 190°C.

Temperature (°C)	Time (min)	Conversion by ^{1}H NMR[b] (%)	M_n[a] (g/mol)	[catalyst]°/ [initiator]°/ [monomer]	M_p[a] (g/mol)	$Đ_M$[a]
170	5	64	39,000	1/0/400	63,000	1.61
190		72	33,000		61,000	1.73
170	15	76	38,000	1/0/400	64,000	1.70
190		80	27,000		56,000	1.95
170	30	80	41,000	1/0/400	66,000	1.66
190		90	24,000		50,000	2.01
170	45	83	35,000	1/0/400	66,000	1.88
190		92	19,500		49,000	2.3
170	60	85	33,000	1/0/400	66,000	1.94
190		95	18,300		35,700	2.14

[a] by GPC in $CHCl_3$, PS standards, 1 ml.min^{-1}, T = 30°C, [b] by 500MHz ^{1}H NMR

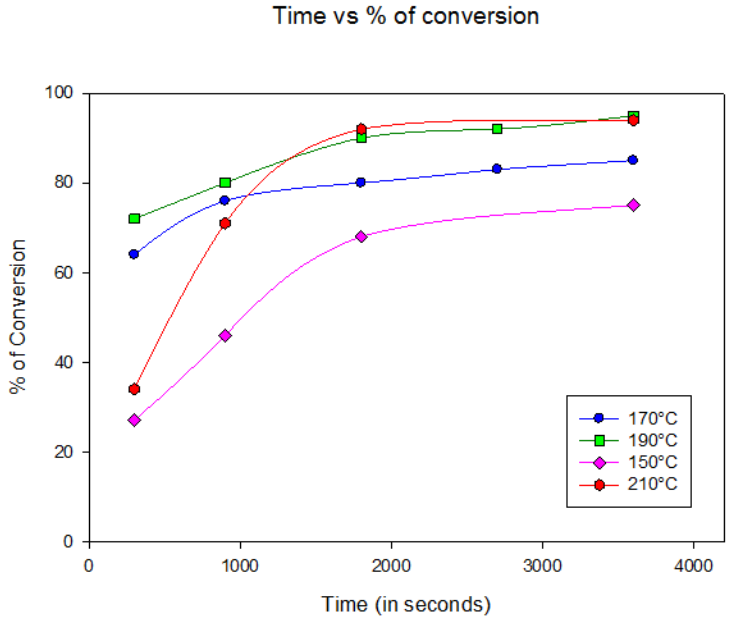


Figure 6: Kinetics of Mg-NHC ROP of L-Lactide without solvent and initiator (alcohol)

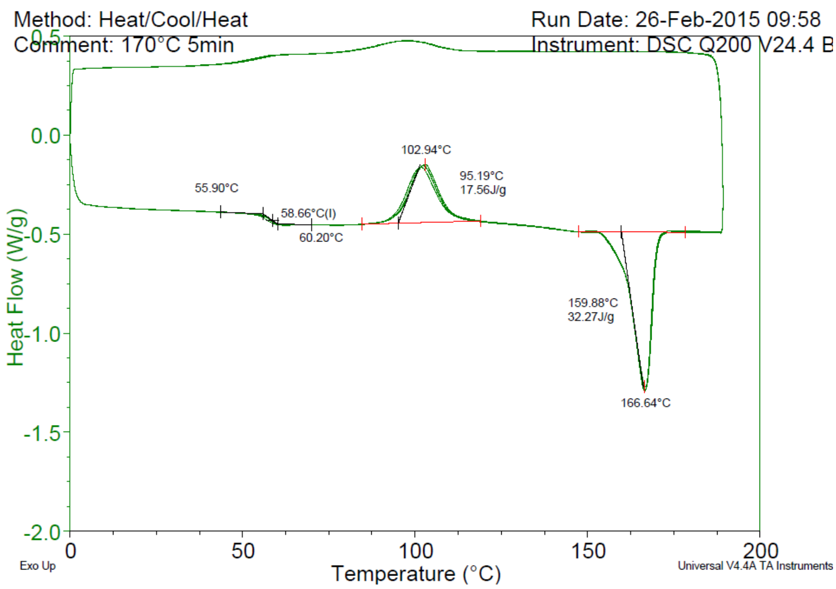


Figure 7: Five-cycle DSC analyses of high molecular weight PLA obtained at 170°C (see Table 1) – from 0 to 190°C at both heating/cooling rates of 10°C/min).

Table 2: Evolution of the extrusion force recorded during the extrusion synthesis of PLA (170°C – 75 RPM).

Time (min)	Force (N)
3*	30
6	40
7	50
8.5	75
9	80
10	85
11	93
12	98
13	100
14	103
15	105
16	108
18	110

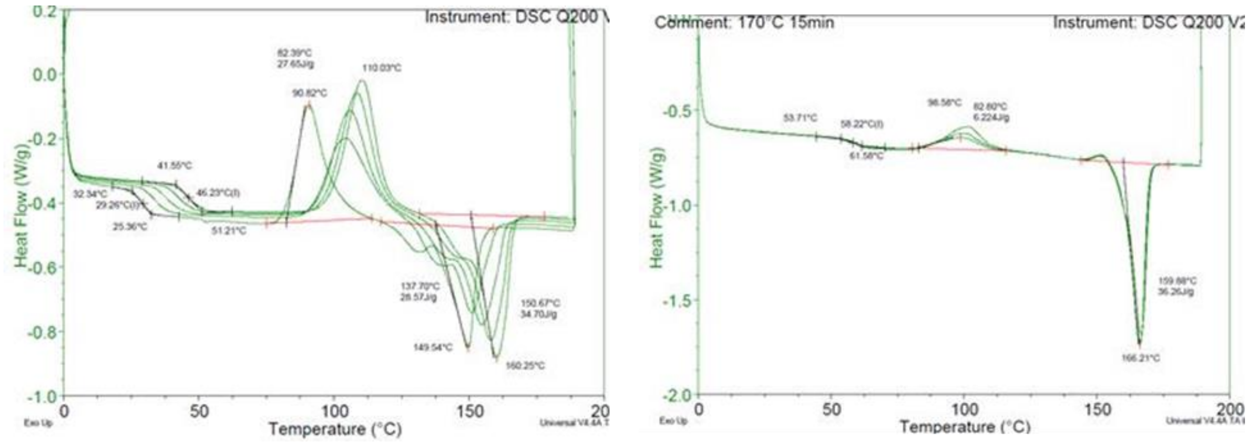


Figure 8: Five-cycle DSC analyses carried out on high molecular weight PLA obtained by extrusion before (a) and after monomer purification (b) (see Table 2 – from 0 to 190°C at both heating/cooling rates of 10°C/min).

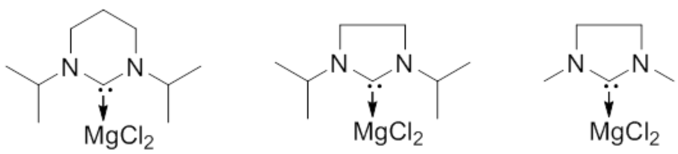


Figure 9: Variation in Mg-NHC

Hielscher: Ultrasonic Polymerization

Figure 10: Ultrasonic lab device UP200St for preliminary tests in smaller scale

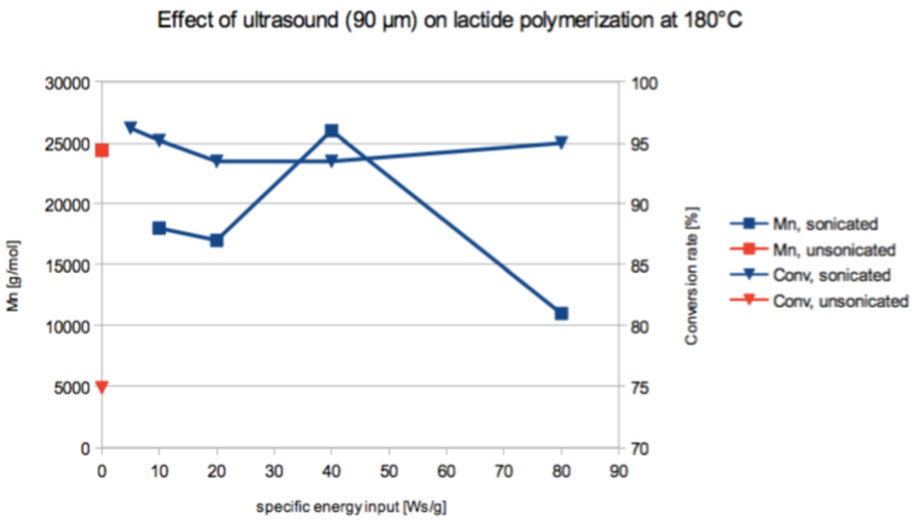


Figure 11: Effects of sonication (90 µm) on lactide polymerization at 180°C

Figure 12: Setup - Ultrasonic batch reactor with pressure sensor and temperature sensor

InsertMPC48 for ultrasonic flow cells

Figure 13: MPC48 with 48 cannulas for fine-size pre-mixing under sonication

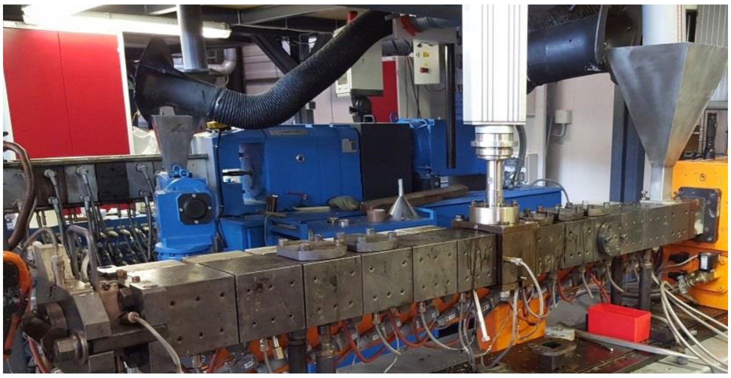


Figure 14: UIP2000hdT on extruder

Figure 15: Extruder block for the integration of the ultrasonic device into the twin screw extruder

Figure 16: Reactor for post-extrusion sonication

MUEGGE: Development, design and setup of an extruder block for injection of microwave energy

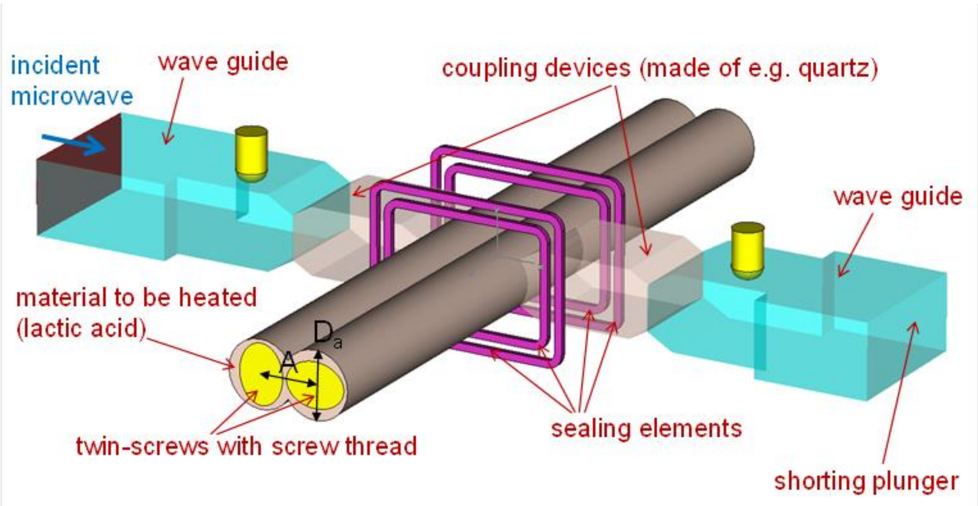


Figure 17: CAD model for coupling of 5.8 GHz microwave to the lab-scale twin screw extruder

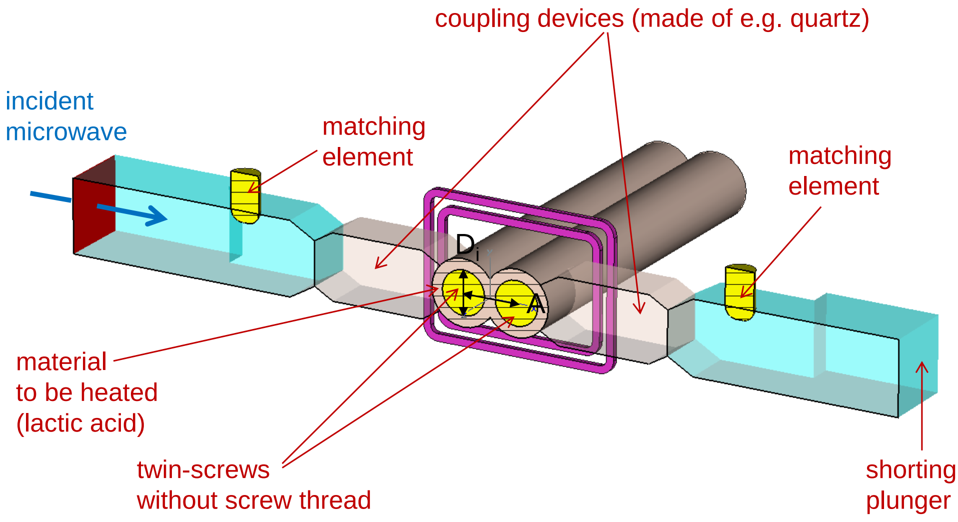


Figure 18: Vertical cross-section alongside the plane spanned by the cylindrical axes of the two matching elements. The diameter of each twin screw without screw thread is D_i = 12 mm, and the distance between the centers of the two screws is A = 15 mm

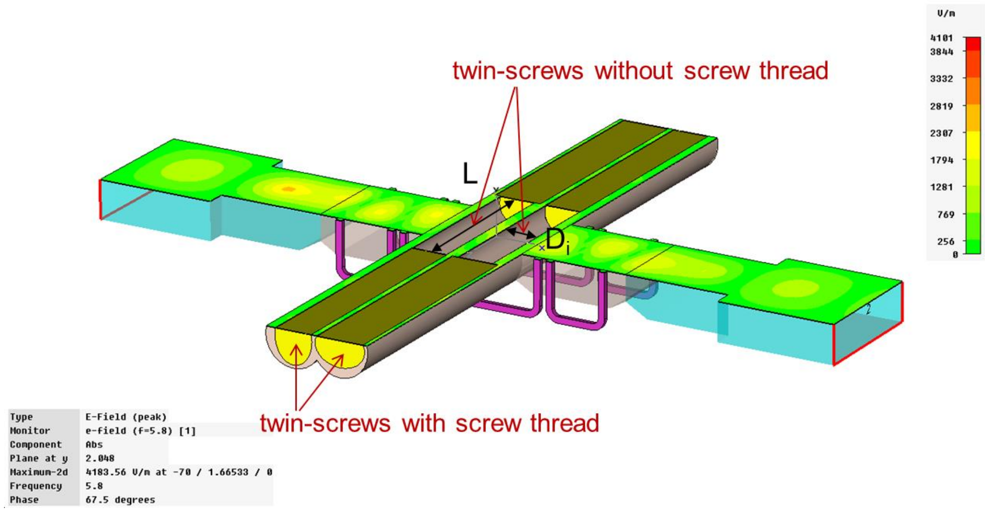


Figure 19: Distribution of the electrical field strength in the horizontal plane

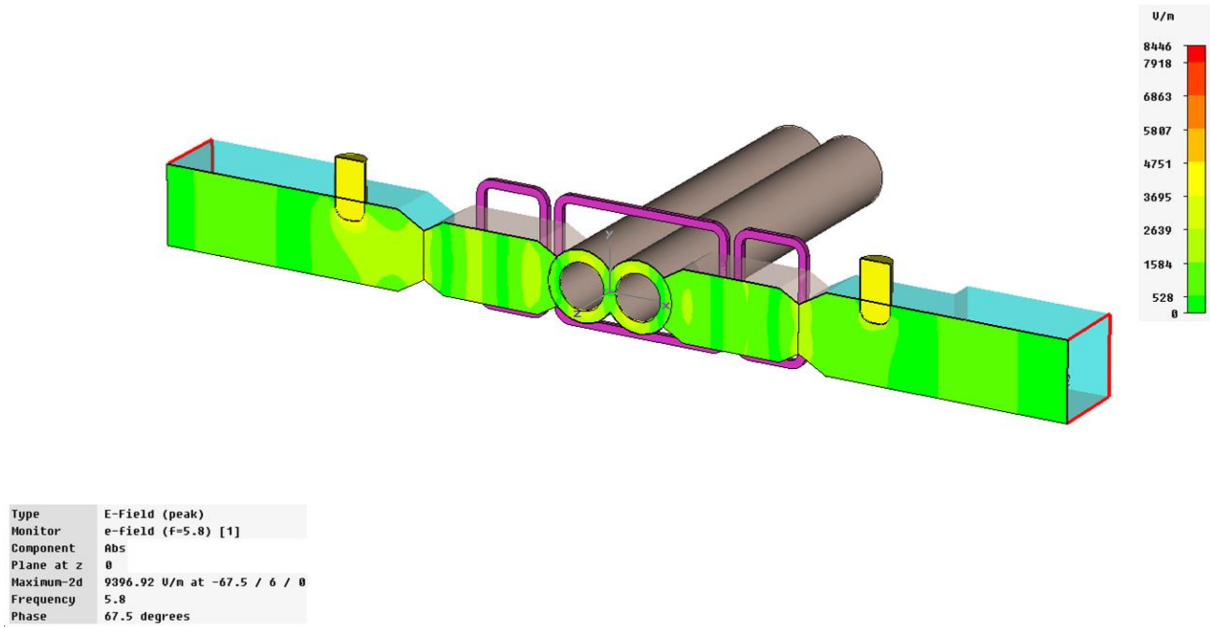


Figure 20: Distribution of the electrical field strength in the vertical plane

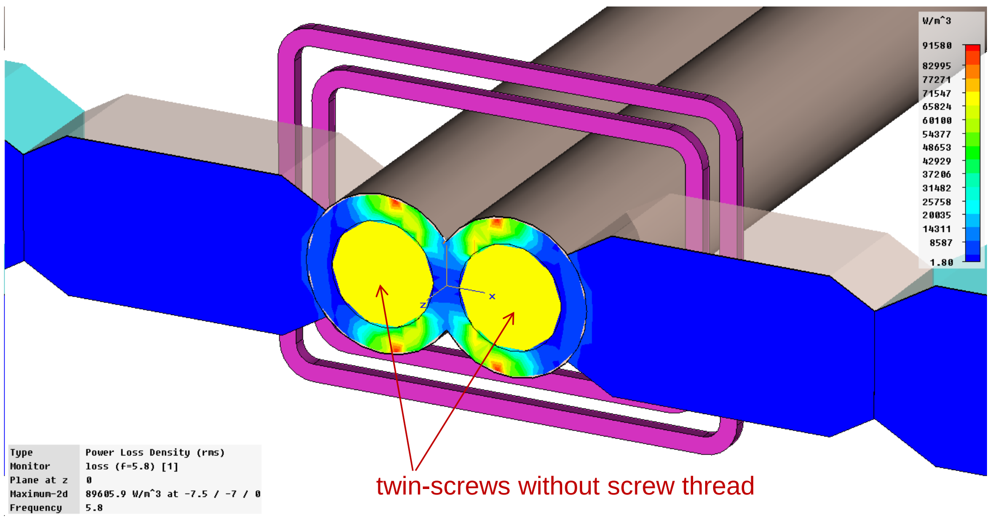


Figure 21: Distribution of the power density in the vertical plane corresponding to the vertical cross-section alongside the plane spanned by the cylindrical axes of the two matching elements

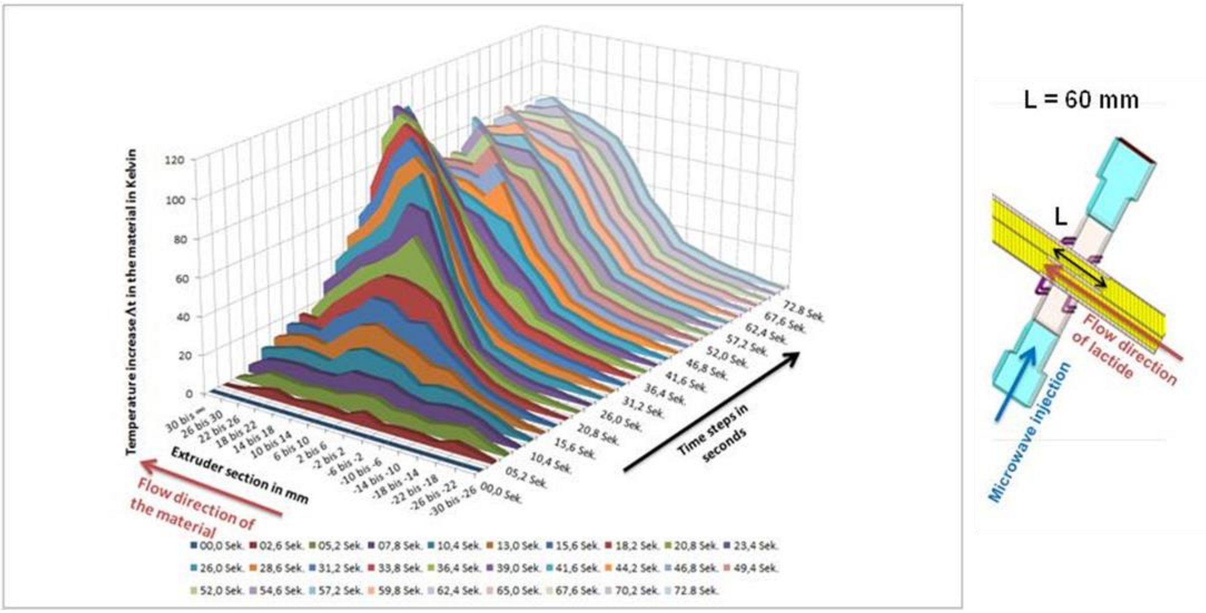


Figure 22: Time-related temperature profiles of the lactic acid in the extruder block for microwave injection

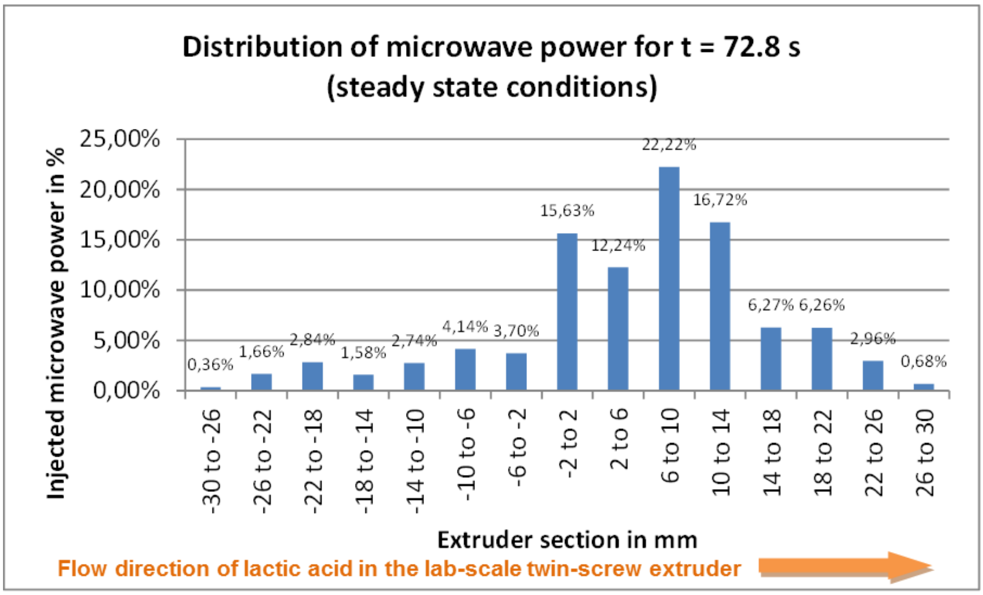


Figure 23: Results obtained from the simulations for the distribution of the microwave power in the different sections of the extruder block for injection of the 5.8 GHz microwave into the lab-scale twin screw extruder at Fraunhofer ICT at steady state conditions

Figure 24: Extruder block designed for microwave injection into the lab-scale twin screw extruder, connected to the shorting plunger on the right and to the E/H tuner on the left (only partly visible) of the 5.8 GHz microwave injection line

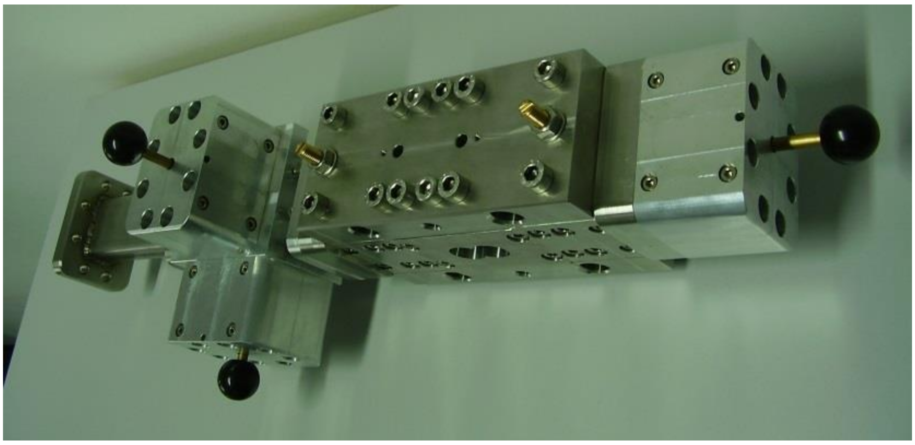


Figure 25: 5.8 GHz microwave injection line including (from left to right) a short piece of R 58 rectangular waveguide, an E/H tuner, the extruder block designed for microwave injection into the lab-scale twin screw extruder, and a shorting plunger

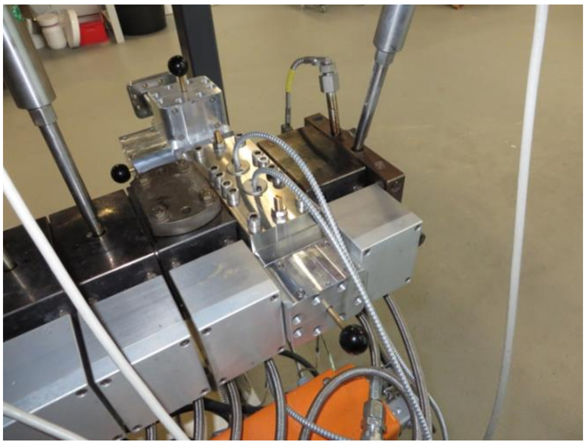


Figure 26: 5.8 GHz microwave injection line including a short R 58 rectangular waveguide, an E/H tuner, the extruder block and a shorting plunger, integrated into the lab-scale twin screw extruder at Fraunhofer ICT

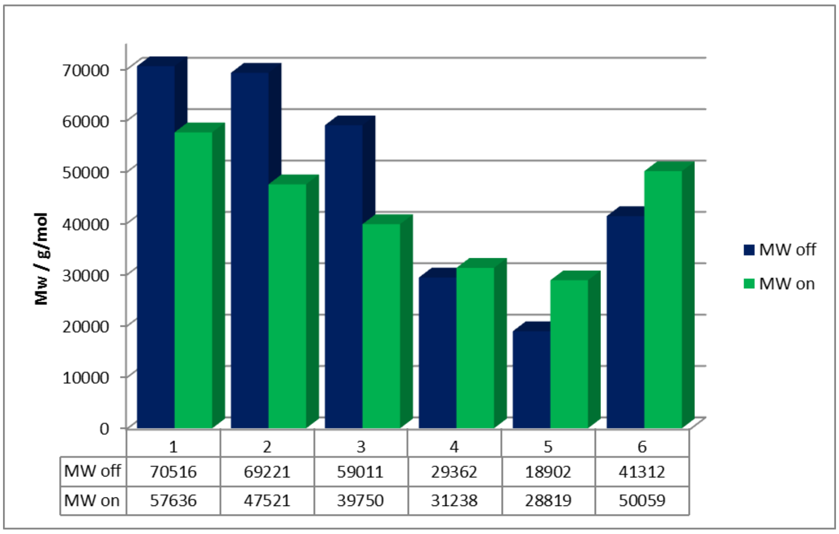


Figure 27: Molecular weight of the resulting PLA obtained for different process settings, with and without application of additional microwave energy injection

Gneuss: Degassing extruder and online viscometer development

Figure 28: Prototype of MRS lab size extrusion system built during InnoREX

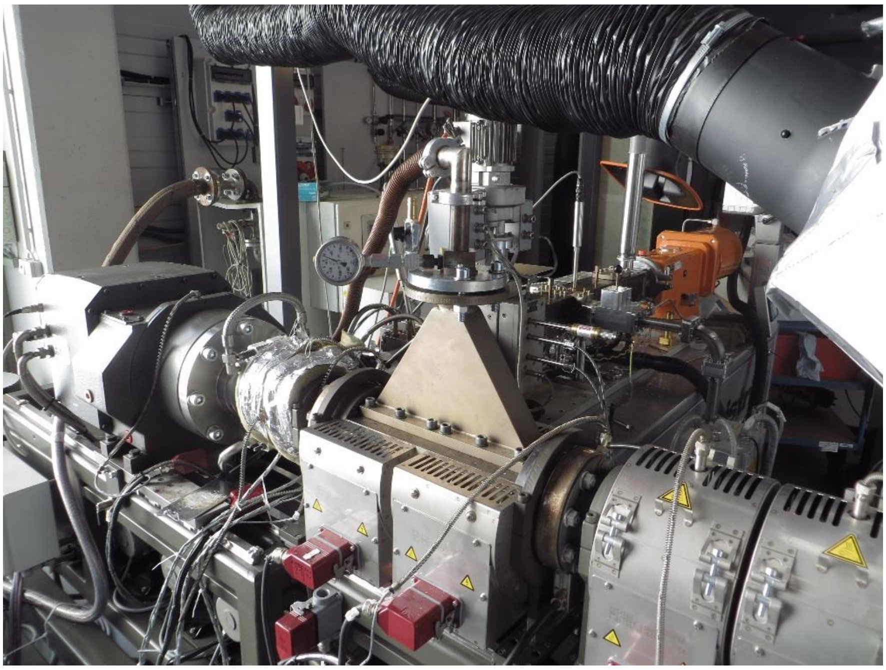


Figure 29: Melt fed MRS de-volatilization system connected to ICT twin screw extrusion system

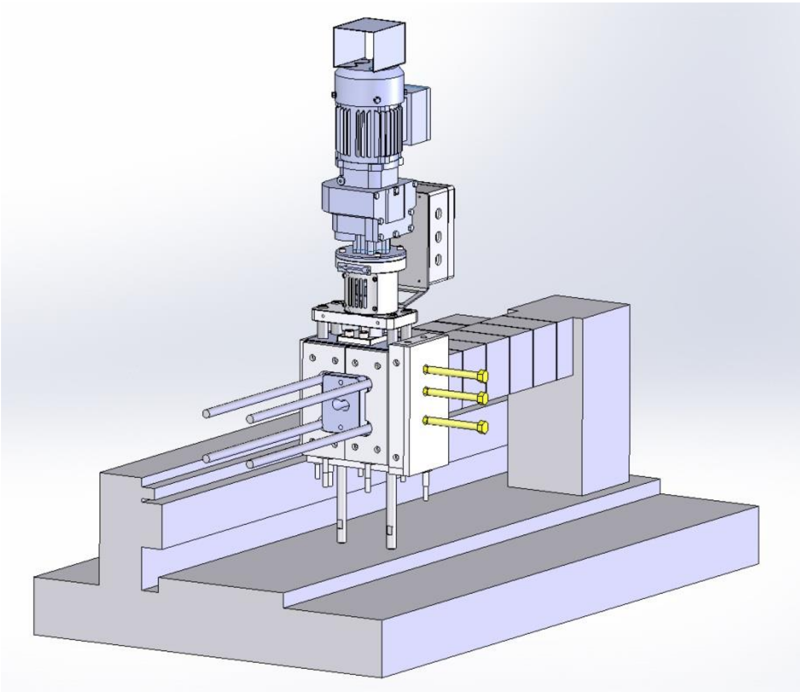


Figure 30: Schematic of extruder integrated viscosity sensing unit

Fraunhofer ICT: Project coordinator combining the InnoREX production line

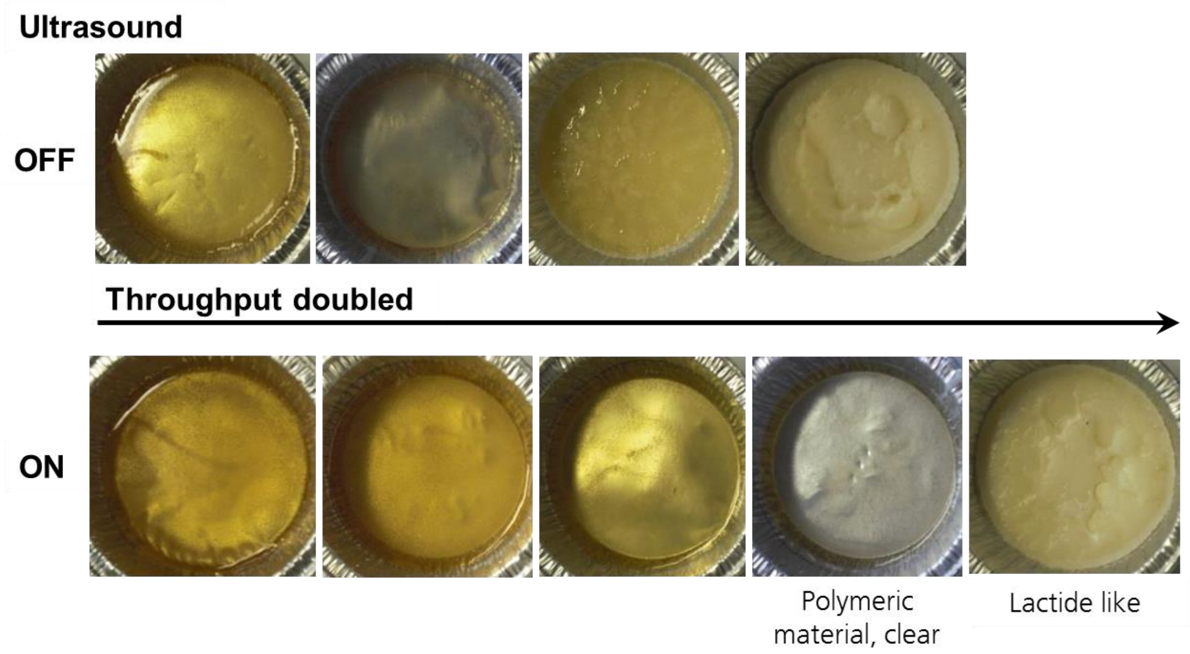


Figure 31: PLA samples produced at different settings with and without incorporated ultrasound energy

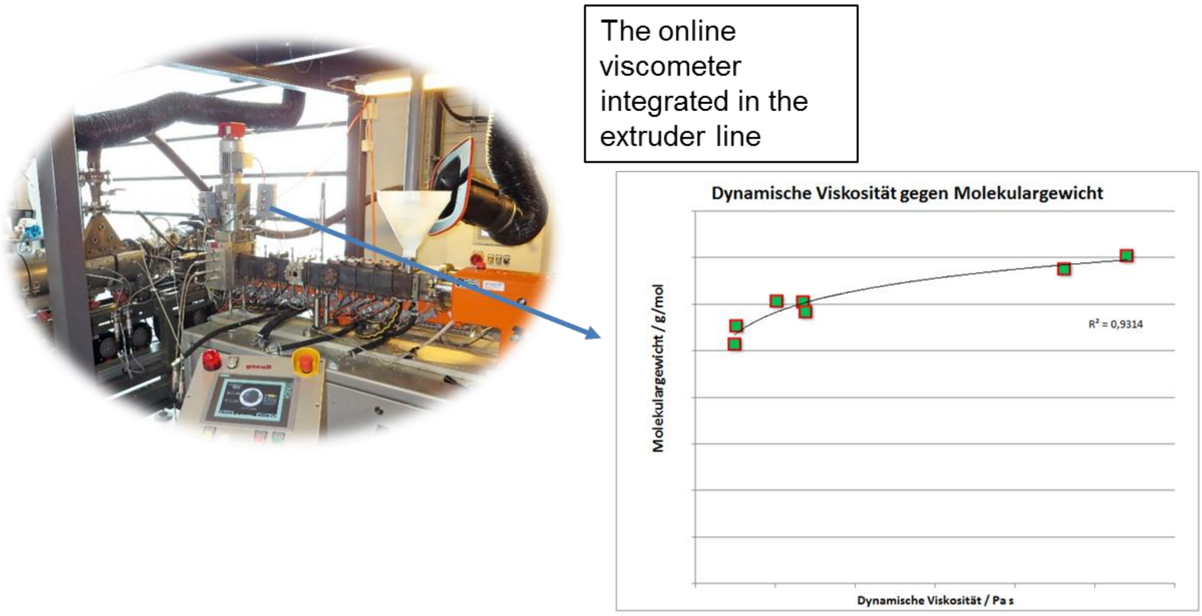


Figure 32: Online viscometer attached in processing length of twin screw and recorded dynamic viscosity with respect to molecular weight

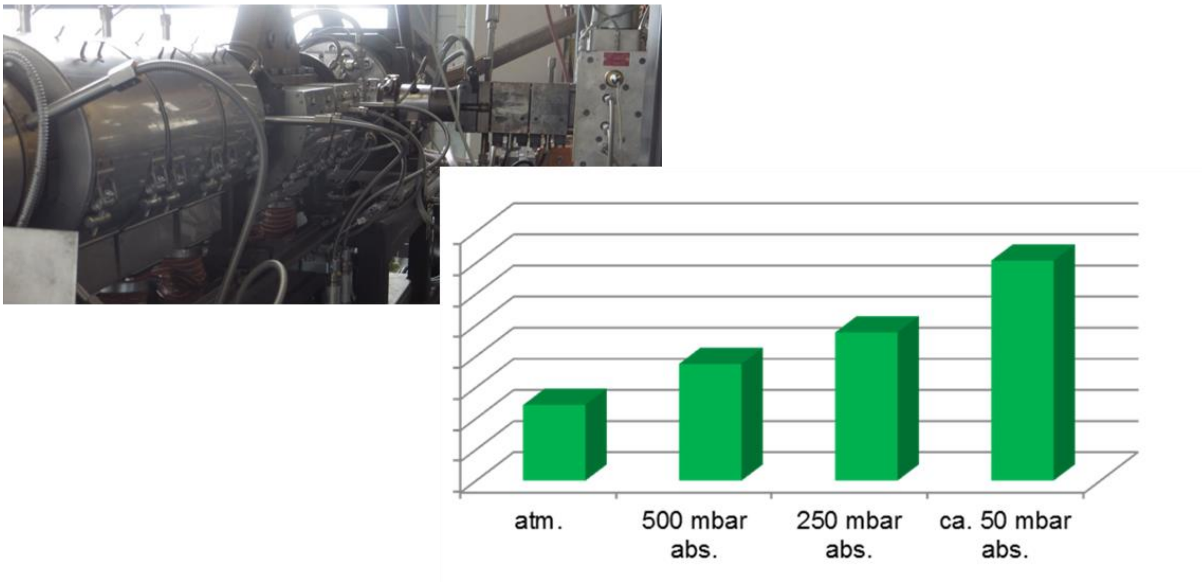


Figure 33: MRS purification extruder attached to twin screw and resulting molecular weights with varying vacuum level in MRS

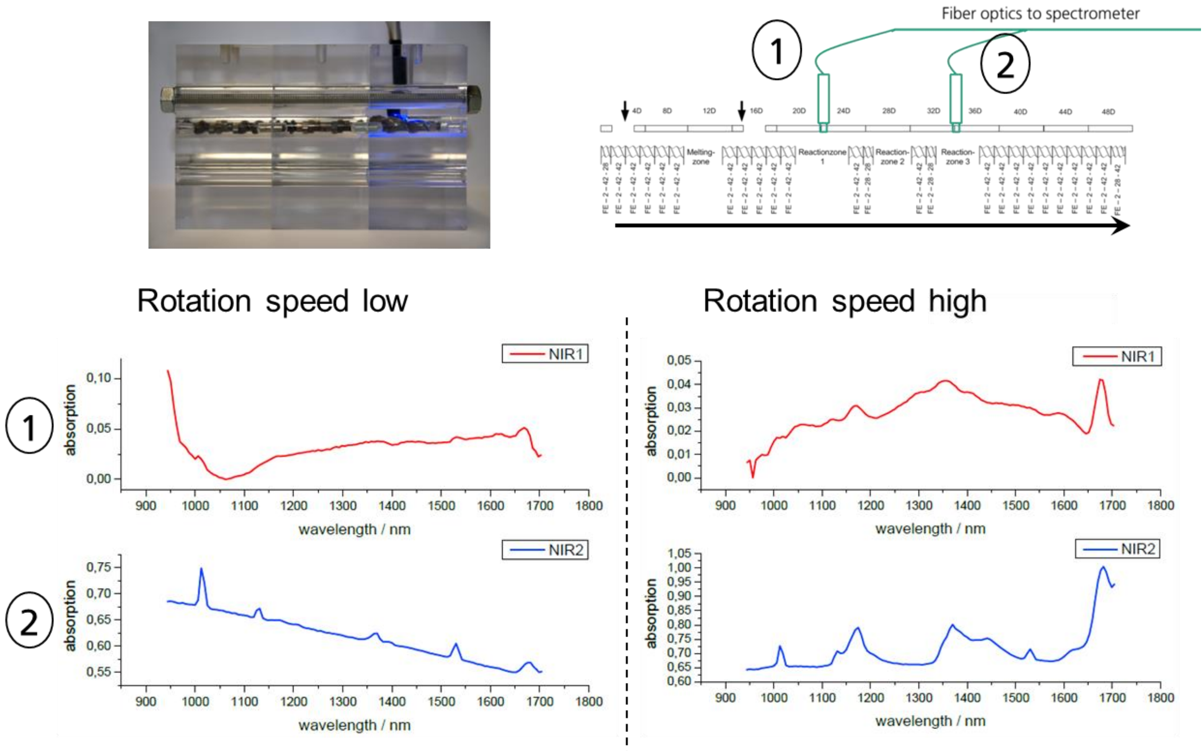


Figure 34: NIR measurement at different points within the processing length and resulting spectra with varying machine process settings

Cranfield University: Selection of simulation technique for understanding of molecular interaction and simulation of most suitable reaction mechanism:

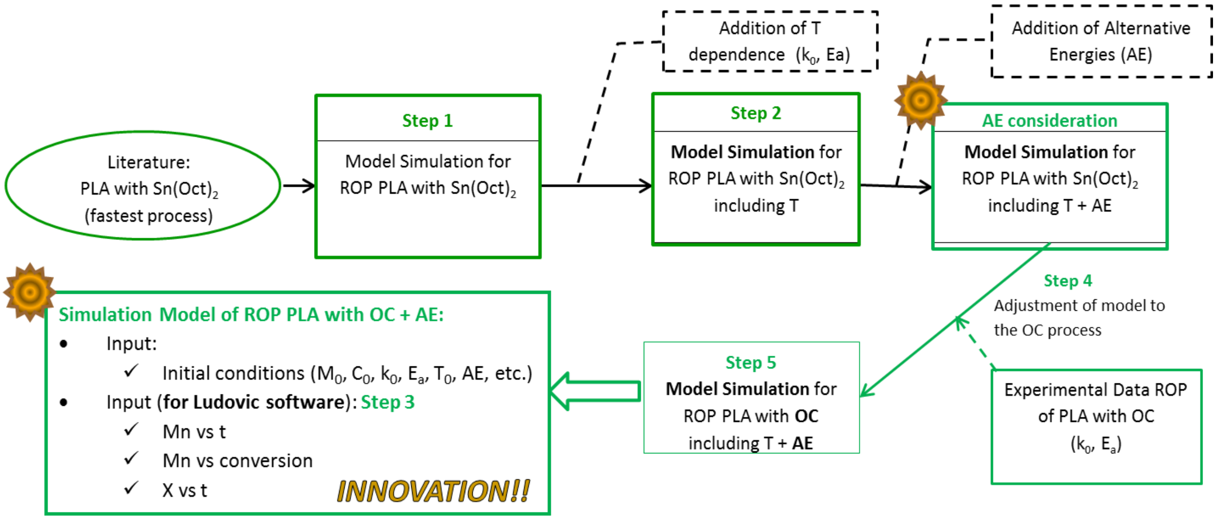
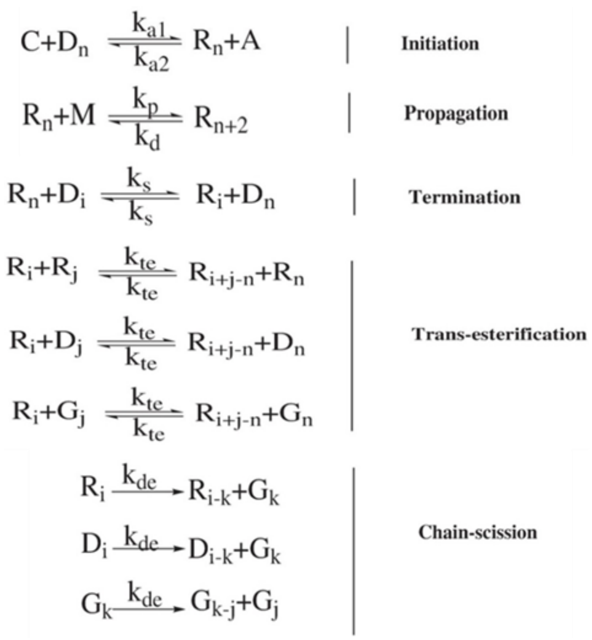


Figure 35: Project work methodology



Where: *ka_1, ka_2 are the activation rate coefficients,*

k_p, k_d are the propagation rate coefficients,

ks is the chain-transfer rate coefficient,

k_{te} is the trans-esterification rate coefficient and

k_{de} is the random chain scission reaction rate coefficient;

C is the catalyst, $Sn(Oct)_2$,
A is octanoic acid (OctOH) produced by the catalyst,
R_i represents the active polymer chains with length "i",
D_i represents the dormant polymer chains with length "i",
G_j represents the terminated polymer chains with length "j" and M the monomer

Figure 36: details of the new five stage reaction mechanism[1]

[1] Yu et al. Ind. Eng. Chem. Res., vol. 50, no. 13, pp. 7927–7940, Jul. 2011

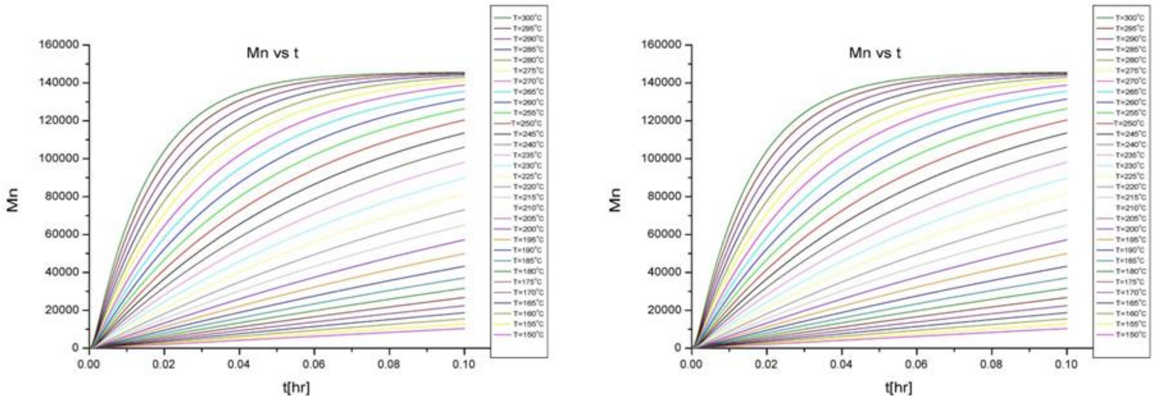


Figure 37: Isothermal curves for conversion (X) vs t and average molecular weight ($\overline{M_n}$) vs t

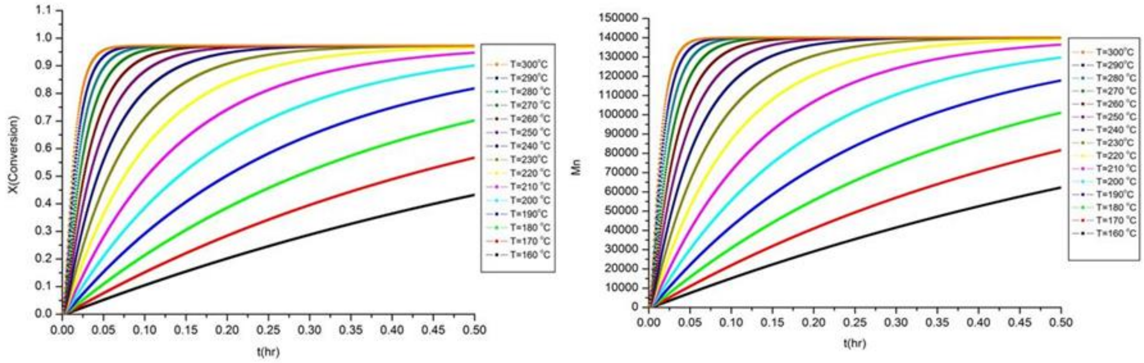


Figure 38: Isothermal curves for conversion (X) vs t and average molecular weight ($\overline{M_n}$) vs t

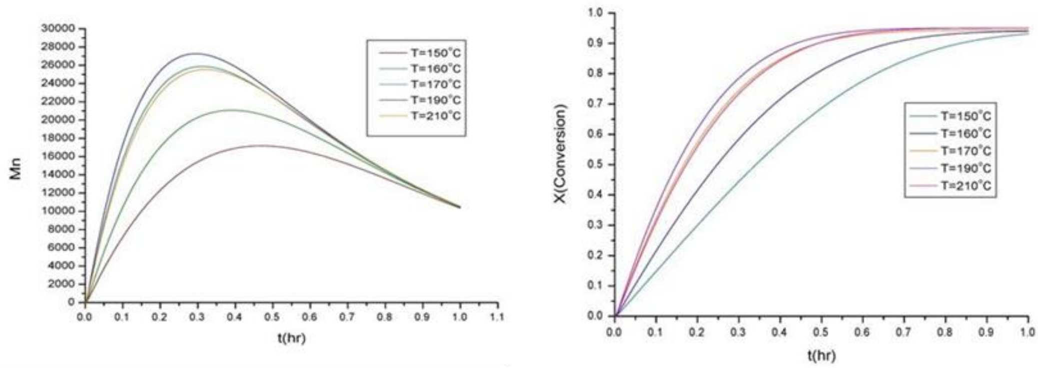


Figure 39: Isothermal curves for average molecular weight ($\overline{M_n}$) vs. t. and for conversion (X) vs. t.

SCC: Totally dedicated to simulation

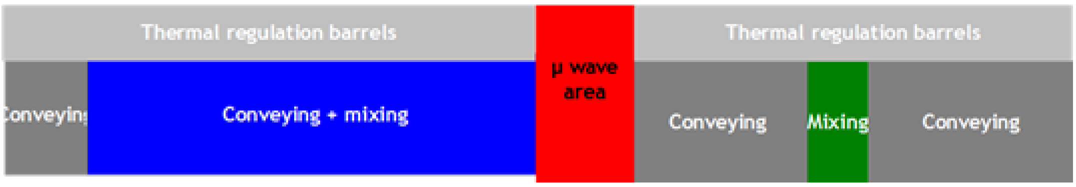


Figure 40: Screw profile with microwave device

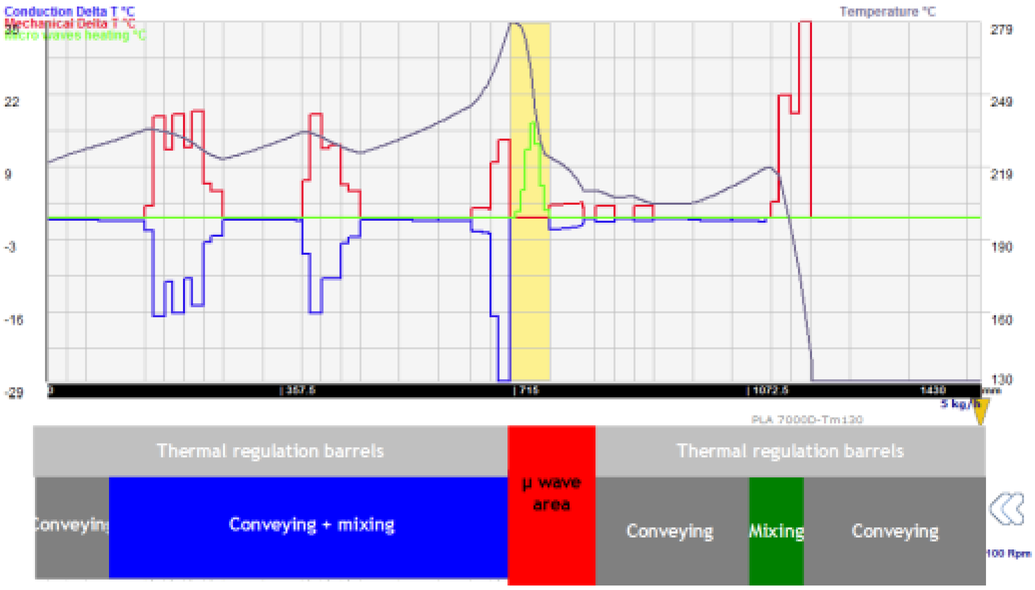


Figure 41: Temperature variation due to conduction (blue), mechanical (red) and micro-wave (100W) (green) effect and result on final temperature (grey)

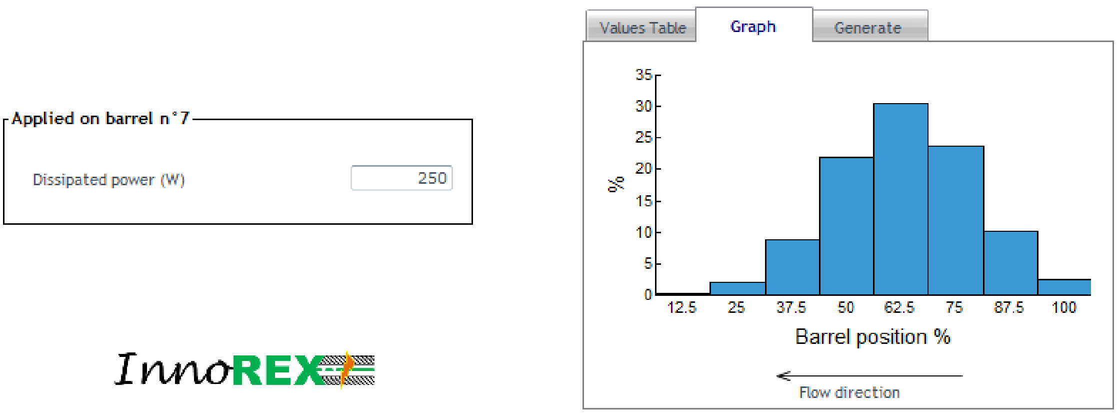


Figure 42: Microwave power Gaussian distribution

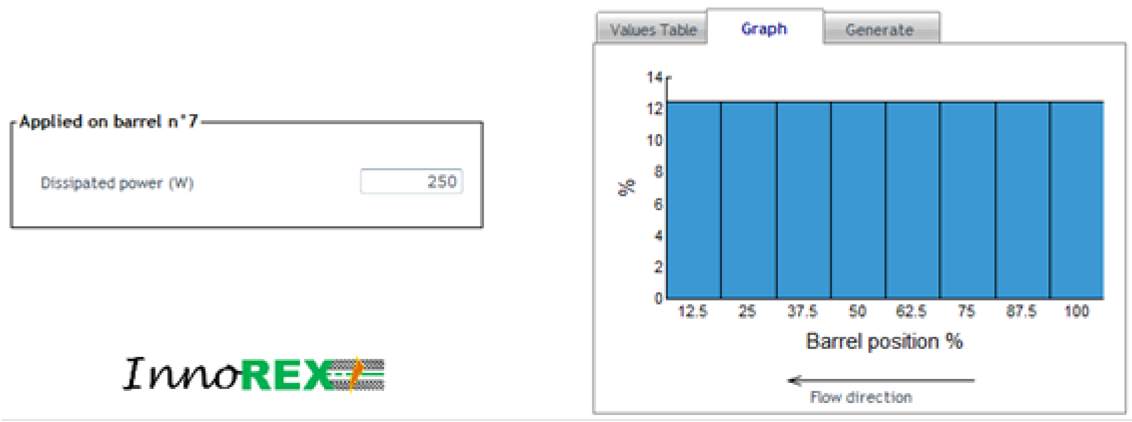


Figure 43: Microwave uniform power distribution

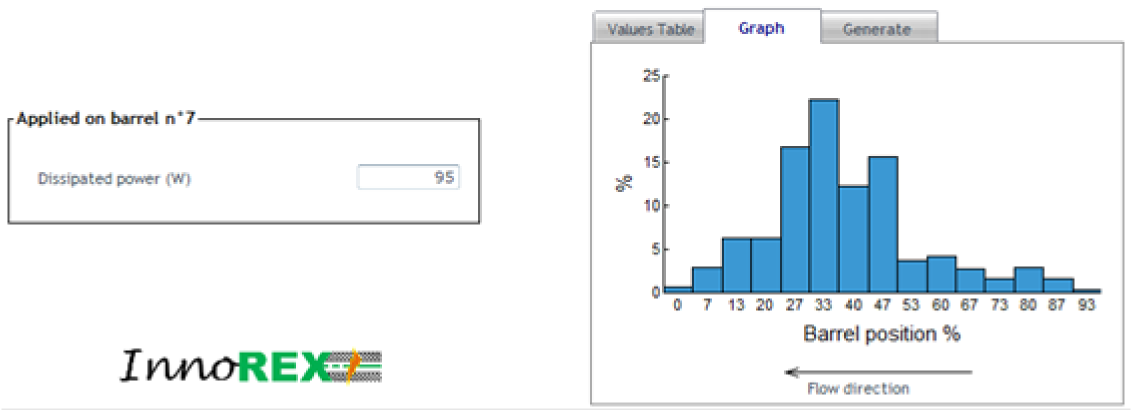


Figure 44: Microwave distribution by user defined (data from MUEGGE)

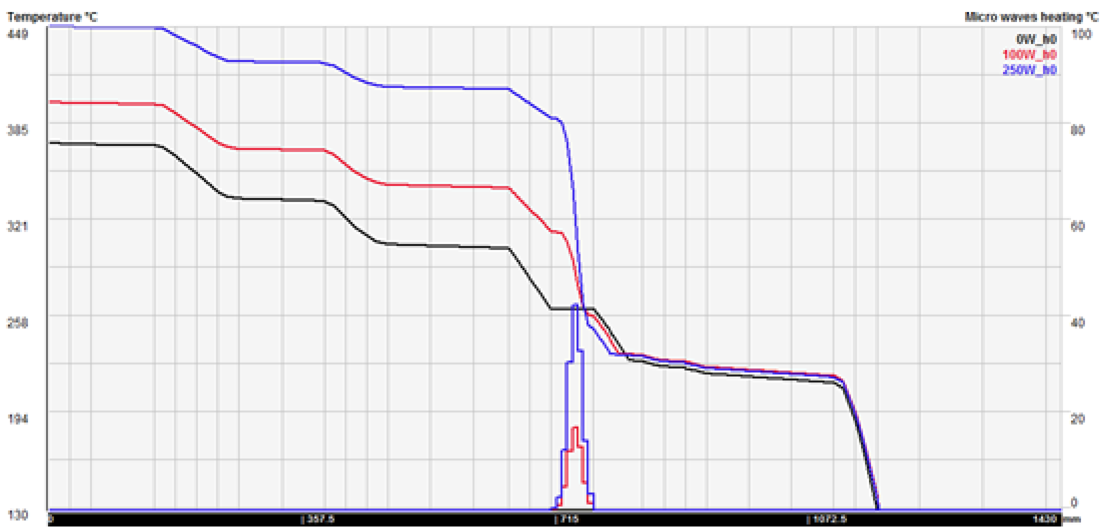


Figure 45: Effect of level of microwave power on temperature

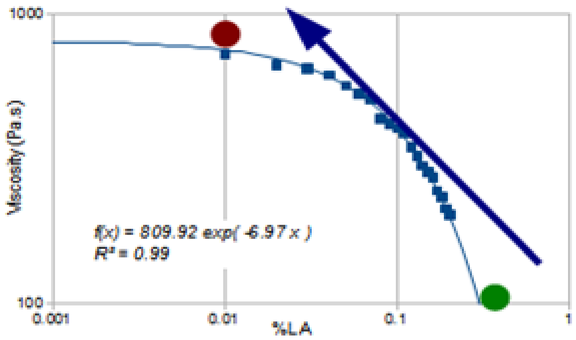


Figure 46: Evolution of viscosity as a function of %LA (curve and trend analysis)

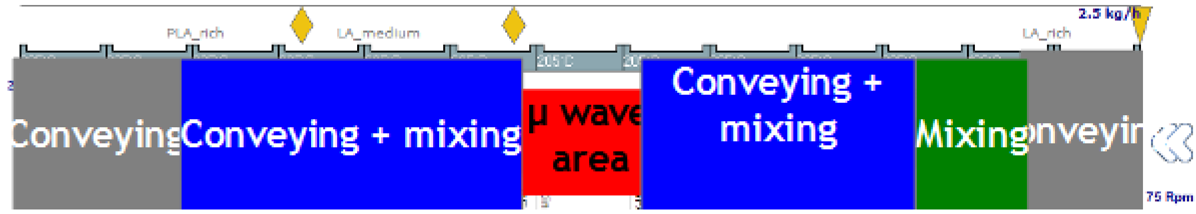


Figure 47: Ludovic® configuration with transition zones

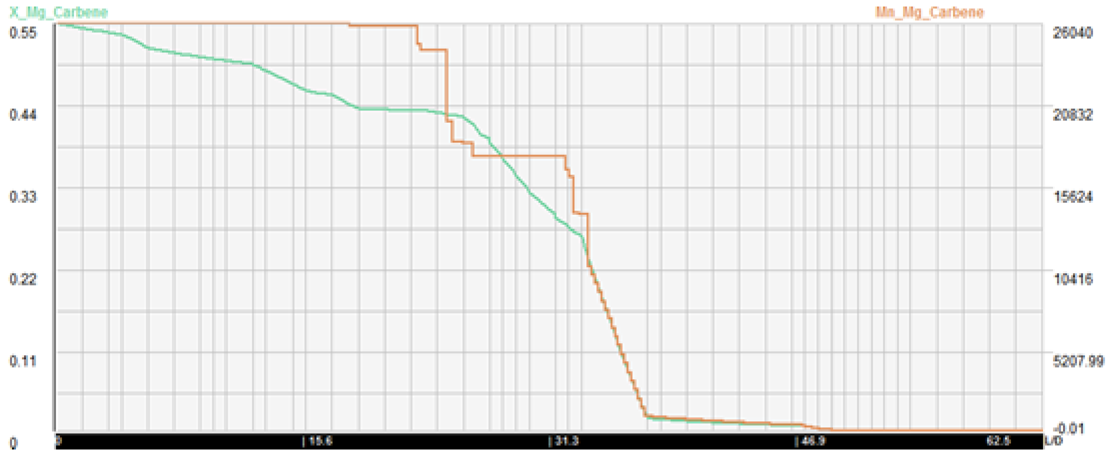


Figure 48: Simulated conversion rate and molecular weight

Materia Nova: Life Cycle Assessment (LCA) study all along the InnoREX process.

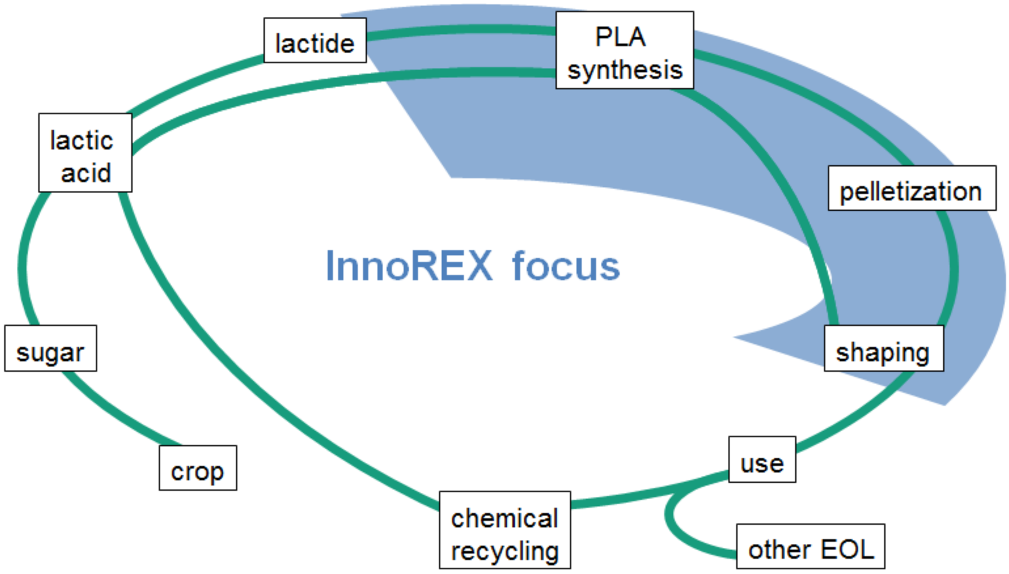


Figure 49: Highlight of the PLA life cycle steps where InnoREX innovations could provide environmental benefits

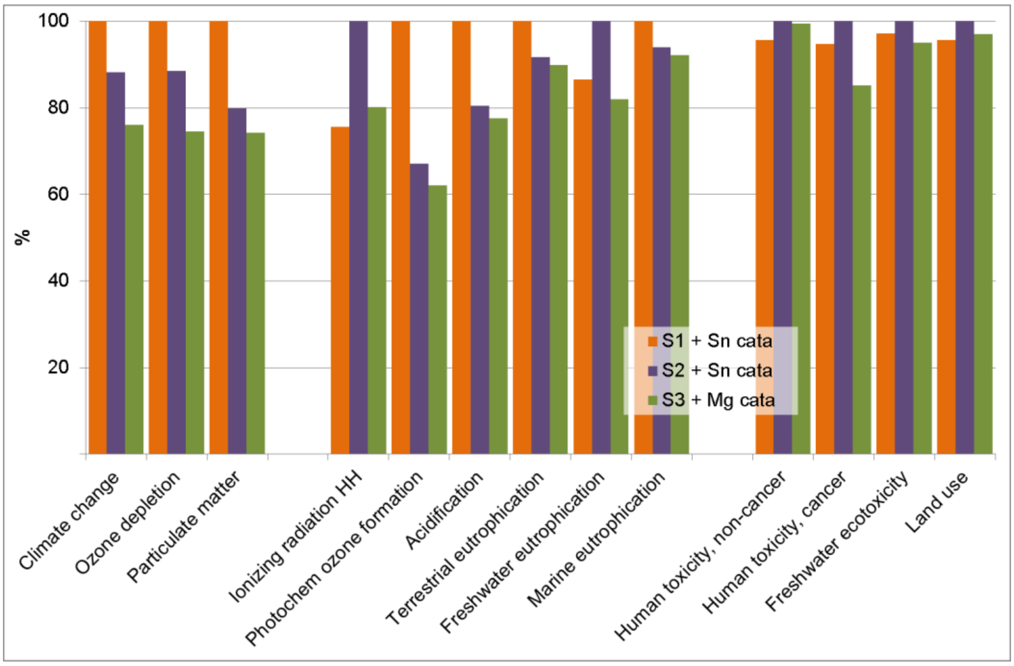


Figure 50: Compared global life cycle impacts for the three scenarios, including catalysts production and catalyst residues emissions.

AIMPLAS: Processability of new PLA grades, mainly focus on manufacturing processes: injection and extrusion.

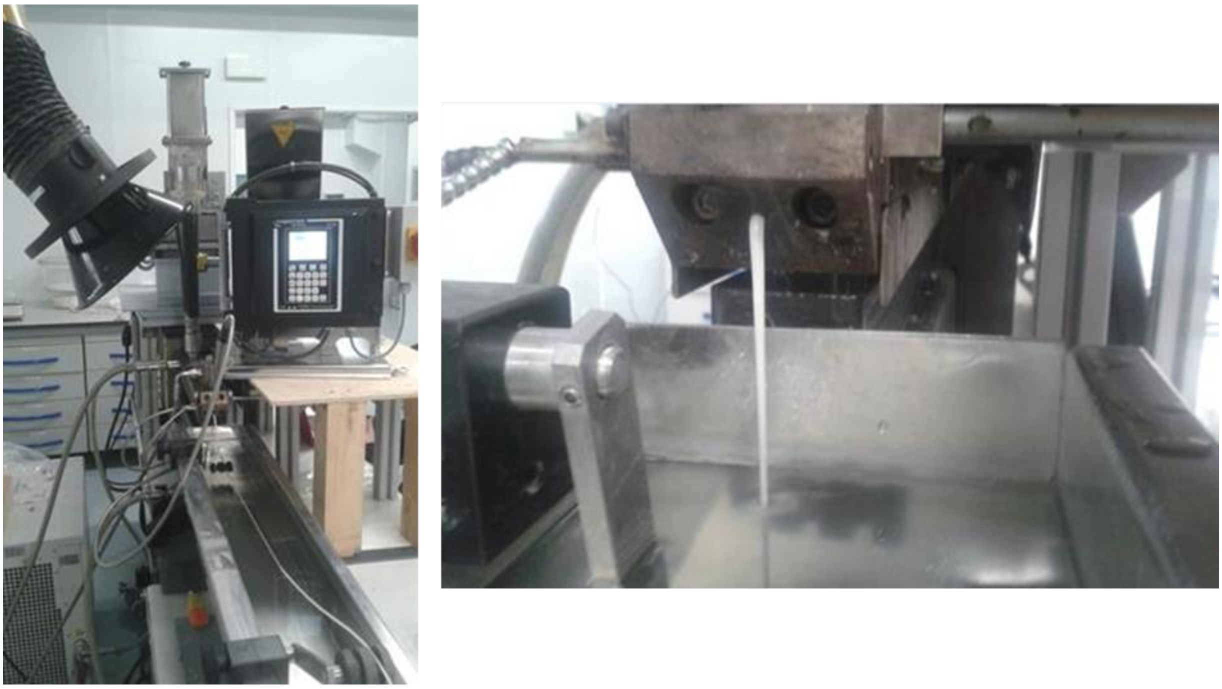


Figure 51: InnoREX PLA formulation during compounding process

Figure 52: Pure InnoREX PLA and additived PLA compound

Figure 53: Cast-sheet extrusion and test bar injection of additived InnoREX PLA compound

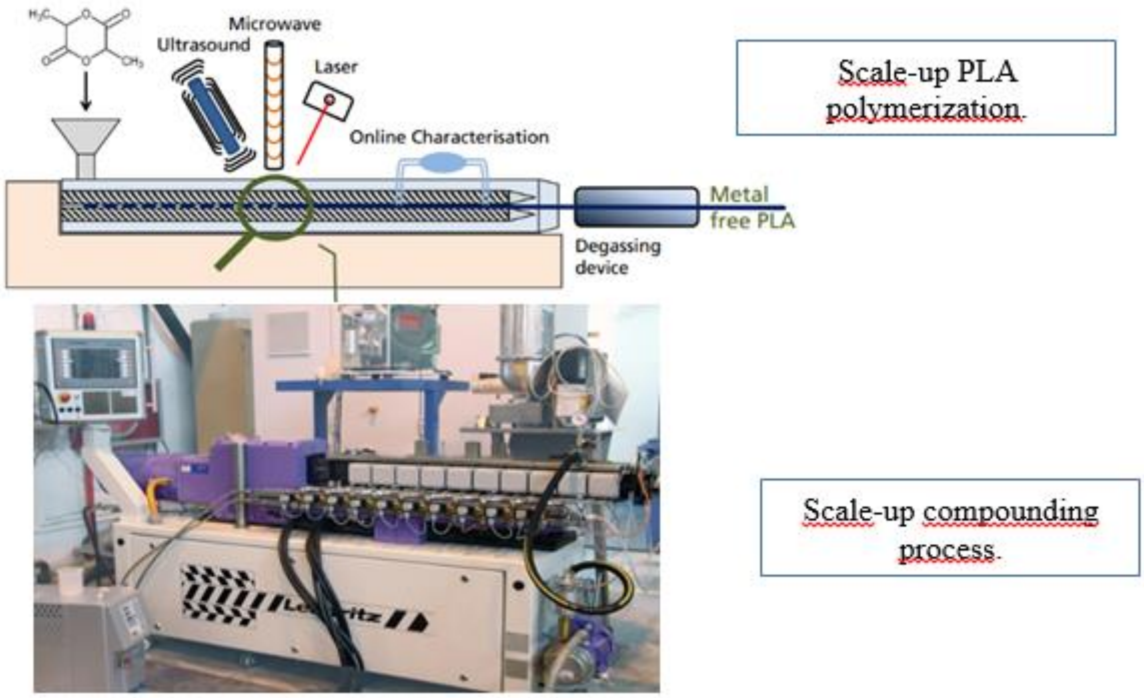


Figure 54: scale up strategy in two steps in order to study both polymerization and compounding scale up

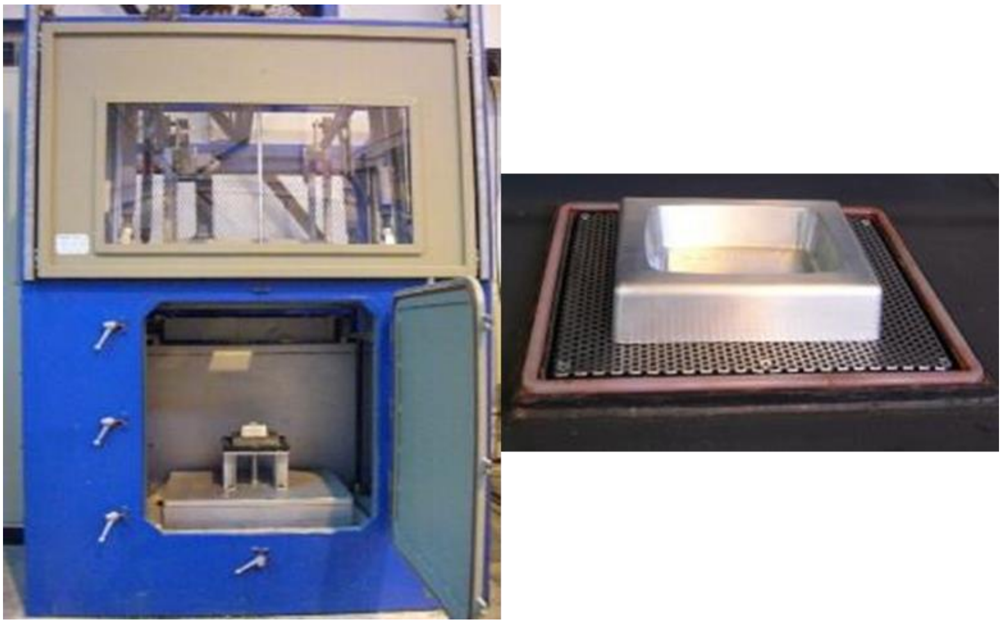


Figure 55: Thermoforming equipment and aluminum mould

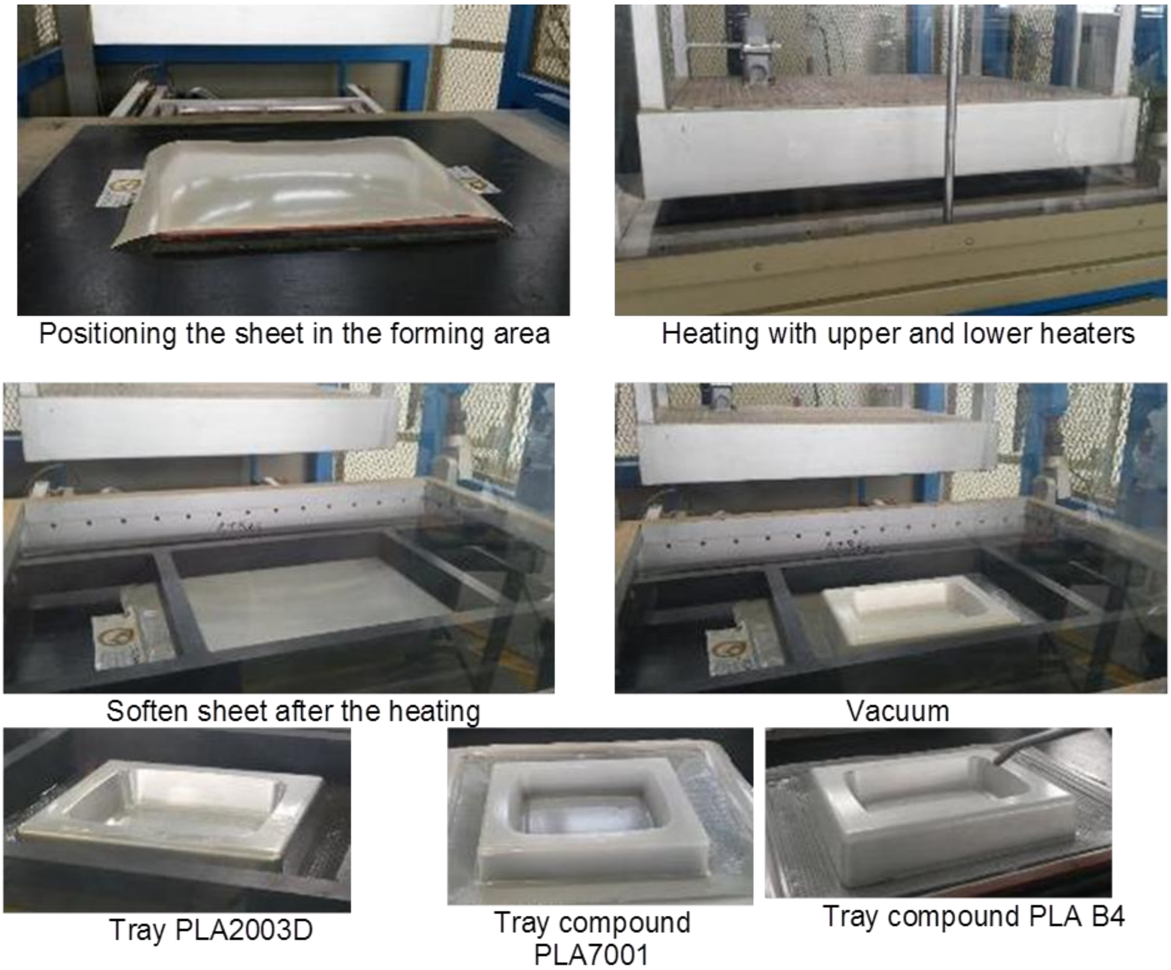


Figure 56: Steps of thermoforming process and final thermoformed trays

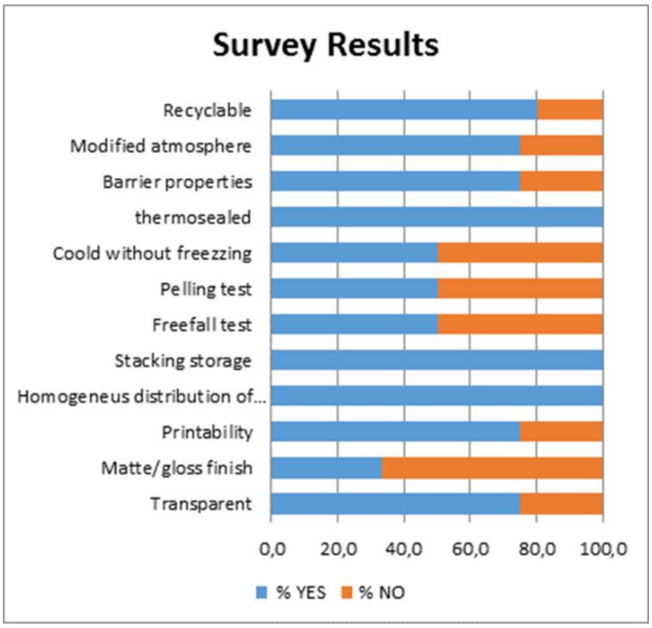


Figure 57: Results from packaging companies of the done survey by Talleres Pohuer

Talleres Pohuer: New PLA grades and case studies thereof mainly focus on manufacturing processes injection moulding.

Photos of packages from InnoREX-PLA

Figure 58: Injection moulded package from InnoREX PLA

BHI – PLA industrial up-scaling

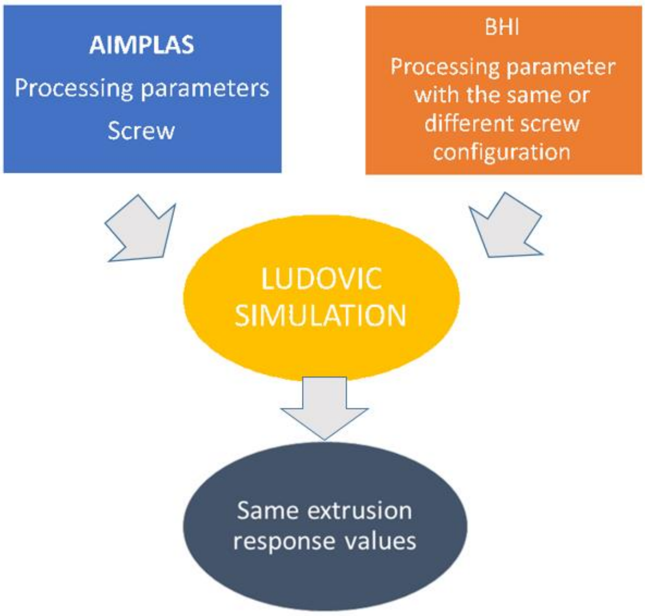


Figure 59: Work methodology of scale up step 1

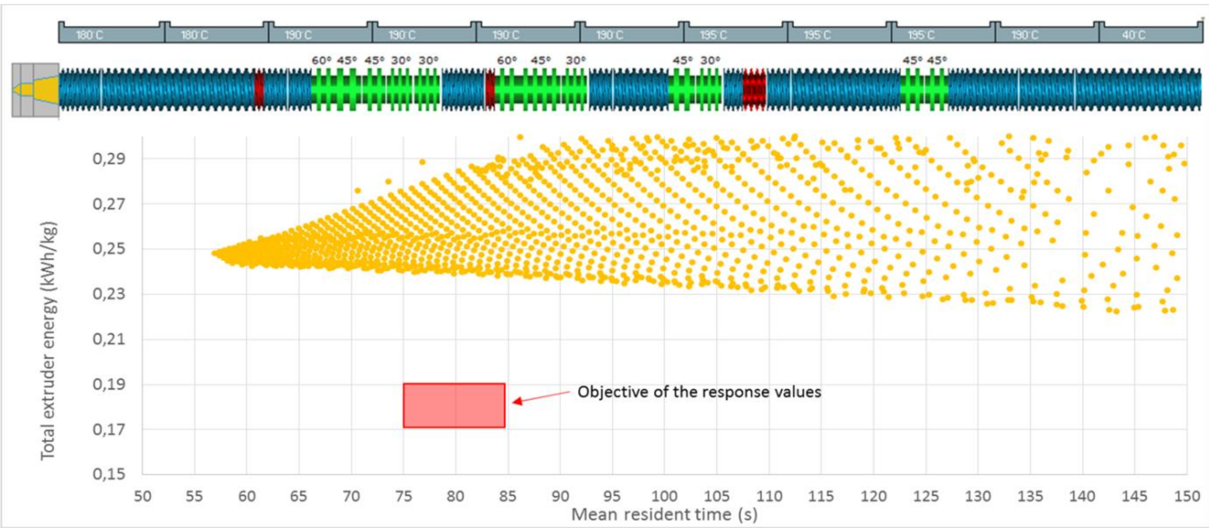


Figure 60: DOE results inputs: Flow rate (50-300kg.h), rotation speed (100-350 rpm)

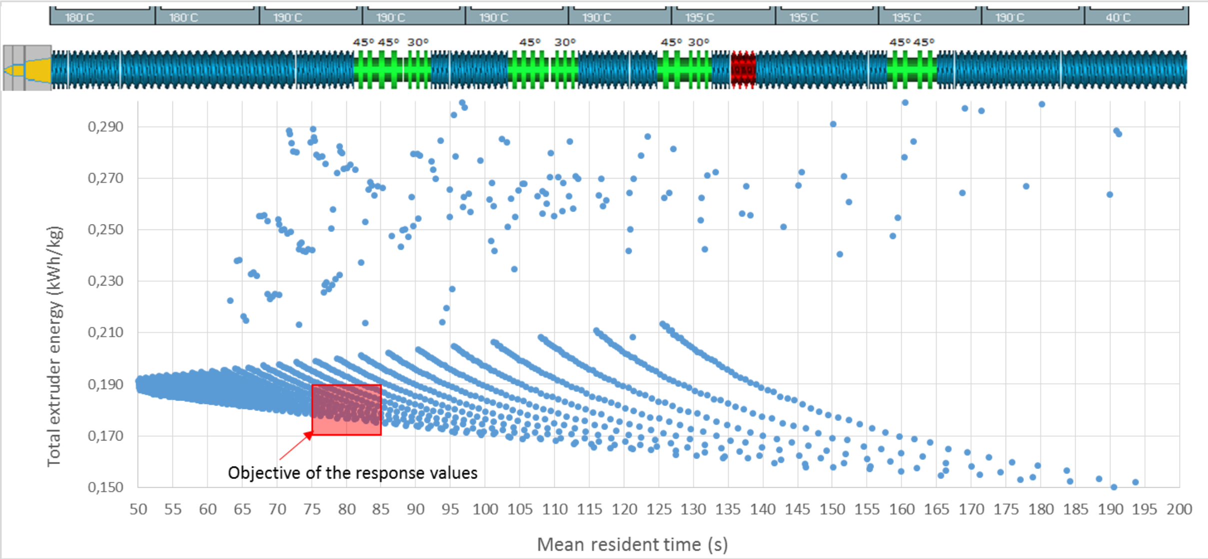


Figure 61: Scale up results with modified screw at temperatures (C) 190-180, throughput (kg/h) 140, rotation speed (rpm) 180

SAMPLE	T_m (°C)	P (bar)	Torque (N/m_2)	Comments
PLA 2003D	186	71	3.0	OK. Thin and thick sheet.
PLA 7001D	186	76	2.8	Un-melted/gels particles
PLA 7001D	201	52	2.4	Few un-melted/gels particles
PLA 7001D + 3% chain Extender	203	126	3.5	High viscosity. Low melt strength. It is not possible to get thin sheet. Only possible thick sheet.
Mix InnoREX PLA	155	9	1.7	Very low pressure. High fluidity. It is not possible to feed constantly the die. Un-melted particles

Figure 62: Extrusion parameters of extrusion studies

Gender dimension of InnoREX project

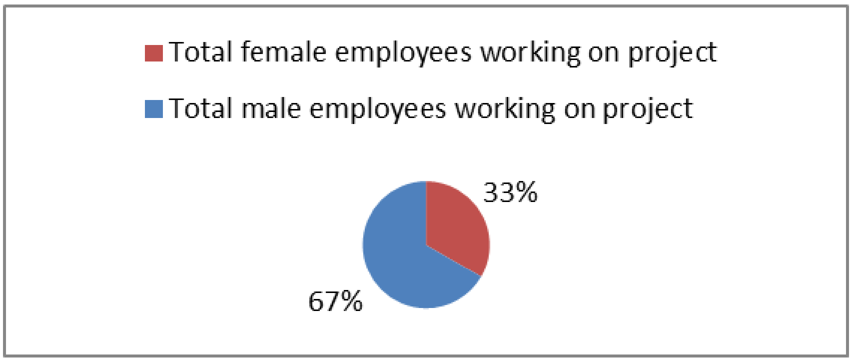


Figure 63: Overview of female and male employees in InnoREX project

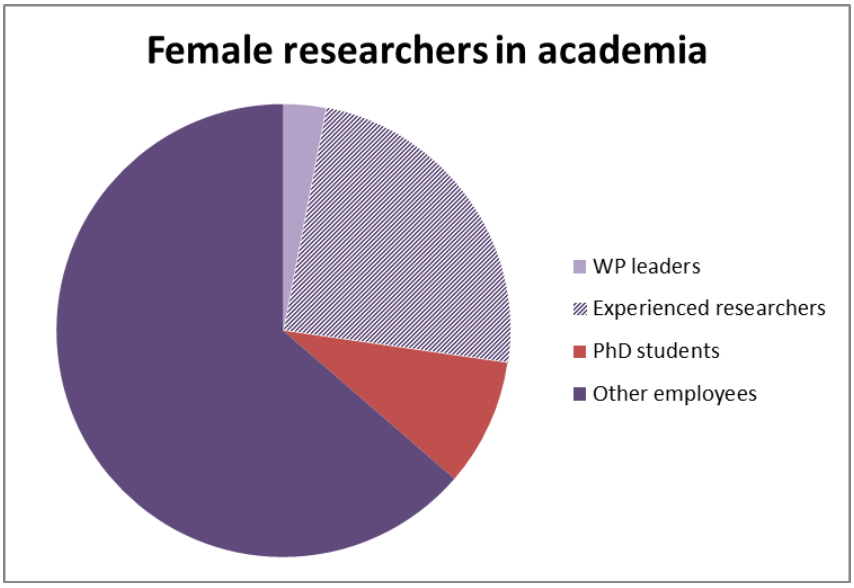


Figure 64: Distribution of female employees in academia