Continuous, highly precise, metal-free polymerisation of PLA using alternative energies for reactive extrusion

**Reporting**

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**This project is featured in...**
Final Report Summary - INNOREX (Continuous, highly precise, metal-free polymerisation of PLA using alternative energies for reactive extrusion)

Executive Summary:
Demand for bio-based polymers is growing fast, but current production technology may use catalysts containing metal which can be an environmental and health hazard.
Mainly focused on the development of an innovative reactor using alternative energies that allow for a continuous and precise polymerization process, the InnoREX project also developed ecofriendly organic catalysts suitable for this new process.
The project demonstrates methods that enhance the production of polymers allowing for a large scale production at a reasonable price.
The particular polymer used by InnoREX is polylactide (PLA) which is mainly used in food packaging and single use cutlery, among other things. PLA is a polymer built up from long chains based on lactic acid molecules. The lactic acid itself is produced by bacteria which are fed by corn, for example, so the feedstock of the polymer is renewable. Another big advantage of PLA is not only that it is biobased but that it is also biodegradable in industrial composting conditions. This means that when it is disposed at composting plants, the polymer is digested by bacteria ultimately resulting in water and CO2.
InnoREX works demonstrated ways to enhance reaction kinetics, speeding up the process of polymerization using twin screw extruders.
Currently twin screw extruders are not used for polymerization on a large scale, because they are not efficient and precise enough as well as not offering sufficient residence times. But InnoREX worked on overcoming this by using alternative energies microwaves and ultrasound. These techniques can achieve
an enhanced, controlled and efficient polymerization of PLA in a twin screw extruder. The consortium managed to introduce microwaves and ultrasound into the extruder which provide additional highly targeted energy and enhance the reaction. The group also adapted an online viscometer which can continuously analyze the material and tell us how complete the polymerization process is. Additionally a second type of extruder was used to purify the product, improving its quality. Finally the produced materials were optimized and parts were produced from it. A simulative description of the process and an environmental Life Cycle Assessment of the PLA produced according to this process completed this project.

Project Context and Objectives:
As oil scarcity results in instability and rising of the price of oil based raw materials, and since recycled materials are rarely suitable for many high-value applications, the demand for bio-based polymers has been growing. However, due to production processes not yet fully optimized and consisting of many successive batch processes, which also require the application of metal catalysts that may be hazardous and prevent its use in some applications, polylactic acid (PLA) has not yet been fully commercially exploited.

InnoREX has overcome these challenges by developing an efficient, economic and ecologically-feasible production process for PLA. The project developed a novel reaction concept for the continuous, highly precise, tin-free production of PLA via reactive extrusion using the alternative energies microwaves and ultrasound. Conventional co-rotating twin screw extruders have been modified to act as reaction vessels, equipped with the additional input of alternative energies to enhance the polymerization kinetics on the basis of organic catalysts. The alternative energy sources allow a dynamic control of the reaction and the resulting molecular structure of the polymer. An in-line degassing extruder purifies the polymer to remove traces of the remaining catalyst and monomer residues. The efficiency of the complete process has been further increased through online analytics in multiple stages of the reactor and the development of a simulation tool. This combined approach therefore covers development from polymerization to part. By performing small-scale batch reaction trials, catalyst screenings, simulations and continuous high resolution analytics, deep understanding and up-scaling strategies have been developed.

Use of commercially available twin screw extruders as a novel reactor concept
Reactive processes in extruders are attracting increasing interest, as continuous processing offers several advantages over batch processing (including cost-efficiency and energy savings). A further advantage of using extruders for polymer production is their capacity to handle highly-viscous material systems, eliminating the need for any solvent in polymerizations. To perform polymer production in commercially available twin screw compounding systems only minor adaptions to already established hardware are necessary. InnoREX developed a new reactor concept by equipping commercially-available extruders with alternative energy input, online characterization tools and a highly-efficient purification device.

Use of alternative energies for precise, dynamic reaction control
The low intensity but highly-targeted input of alternative energies in the reaction volume ensures a high molecular weight polymerization within the limited residence time of an extruder. For a dynamic control of the reaction, rapidly adjustable energy input is needed. This cannot be achieved by the static energy input of an extruder, but in comparison to an extruder microwaves and ultrasound show nearly no response time. This allows dynamic control of the reaction in the extruder.
Alternative energies also have a significant and highly-differentiated impact on reaction mixtures and polymers. Utilising the different influences of the alternative energies InnoREX showed the possibility to gain a precise dynamic control of the polymerization and the molecular structure (branching, crystallinity, molecular weight, etc.) of the resulting polymer by varying the alternative energies and their modes of operation. For each individual type of alternative energy InnoREX revealed its profile of effects in polymerization reactions and reactive extrusion in general. This allowed the interdisciplinary consortium to utilise the generated knowledge widely beyond the InnoREX project and gain a major technical impact of the InnoREX results and their transferability to other polymerizations, reactive extrusion processes or innovative continuous processes.

Use of metal-free organic catalysts

According to the current state of the art, metal-containing catalysts (e.g.: tin (II) 2-ethylhexanoate) are needed to improve the polymerization rate of lactones to a commercially acceptable level. Health- and environmental regulations dictate that polymer products entering the market must not contain residues of metal catalysts equal or more than 100 ppm. To avoid metal-containing catalysts, organic catalysts have been investigated in the InnoREX project. These catalysts have shown the ability to efficiently control the polymerization of lactide, but yet their performance is insufficient to meet industrial scale standards.

Purification of the InnoREX PLA grade

Purification of the PLA products by removing unreacted monomer strongly influences the stability of the final polymer. This stability is primarily linked to monomer content and catalyst deactivation. InnoREX utilised a specially designed, high-performance MRS extruder type purification device in-line to the polymerization extruder to ensure superior material properties due to high purity. The purification device did not need to incorporate additional high amount of energy in the material (as for heating / melting), and has been able to remove efficiently traces of unreacted monomers and by-products.

Scientific and engineering understanding of the mechanisms behind the alternative energy based processes and of the relations between various parameters influencing those processes

For a deepened understanding of the underlying reaction mechanism the reaction kinetics, the influence of different catalysts and alternative energy sources has been studied thoroughly in small scale batch reactions before realising high throughput continuous polymerizations. In continuous polymerization experiments online analytics have been applied at different stages of the reactor for a deep understanding of all stages of the polymerization. Finally, the resulting polymer has been studied utilising offline chemical analytics and mechanical investigations. Additionally, a Life Cycle Assessment (LCA) study about the new polymer and its production process has been performed, revealing the potential of InnoREX final resulting process for an improvement of the ecologic and economic impact of PLA. Simultaneously the commercially available Ludovic® simulation tool for compounding processes associated to reactive processes has been applied to the simulation of polymerisation reactions identified in academic tasks. The incorporation of additional alternative energy (micro waves) input in twin screw compounding systems has been introduced into Ludovic® thanks to InnoREX project. Additionally, the mechanical interaction between the alternative energy sources, the catalyst and the reaction mixture were studied using molecular dynamics simulation.

Demonstration
A working polymerization line including the incorporation of alternative energy, online characterization technology and a purification device to remove the catalyst has been built up. PLA parts have been produced to demonstrate the different properties of the material which can be achieved by the new process. End-users within the consortium successfully demonstrated these different properties within the case studies: compounding (BHI), extrusion cast-sheet and thermoforming (AIMPLAS), and injection moulding (TaPo). To ensure the projects strategic development to the demands of large scale end-users, additional case studies have been defined strictly by the members of the Industrial Exploitation Board. Furthermore the enhanced Ludovic® software has been described and displayed in dissemination activities showing the potential of the simulation outcome of the InnoREX project.

Project Results:
Université de Mons: Catalyst development for the bulk polymerization of L-lactide

Introduction

There is a perceiving demand of metal-free catalyst development for the bulk polymerization of L-lactide in a controlled manner. For the last few decades metal-free catalysts for ring-opening polymerization (ROP) of cyclic esters such as L-lactide has been the momentum to develop them in solution and in bulk. While many organic catalysts have efficiently promoted the ROP of lactide in solution, there have been relatively few examples that are capable of doing so with a high degree of control under solvent free conditions (bulk) and at high polymerization temperatures (higher than 150 °C). The major issues about these organic catalysts under these conditions are their propensity to promoting undesirable side-reactions such as inter- and intramolecular transesterification reactions and epimerization. In the latter it yields PLA-based materials of low crystallinity features and poor mechanical properties.

Background

Within the InnoREX project consortium UMons developed different catalysts. Among them some of them are active towards bulk polymerization. 4 Dimethylaminopyridine (DMAP) was one of the first organic catalysts, which demonstrated to be capable of catalyzing the ROP of lactide in bulk at 130 °C, although it showed only moderate control under bulk conditions, requiring polymerization times longer. In this respect the combination of DMAP with its conjugated salt(s) of various natures has been considered, resulting in considerable polymerization rate enhancement over DMAP alone for the polymerization of lactide, with a dual activation mechanism proposed (see Figure 1 in attachment).

In this effort among these various conjugate salt pairs with DMAP it resulted with the higher conversion of 54% obtained after 30 minutes. Despite higher monomer conversion, it yielded lower molecular weights and epimerization, i.e. loss of crystalline features of resulting PLA matrices, limiting the use of these catalysts in bulk polymerization. Further work has been undertaken to develop an alternative organic catalyst. Several attempts were carried out and different catalysts were experimented. Among those were 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU), and betaine-type catalyst (see Figure 2 in attachment). Strategies were employed as they were shown to be highly active organic catalysts for lactide polymerizations in solution (Figure 2). Under bulk conditions the catalyst DBU and its conjugated salt combinations however resulted in a significant transesterification extent, leading to a lack of control over the bulk synthesis of polylactide.

For instance, bulk polymerizations were undertaken at a temperature of 130 °C for 30 minutes with increasing amounts of both types of catalyst. Despite high conversion in 30 minutes it again resulted in transesterified and low molecular weight PLA materials. In addition to that high degree of epimerization
was observed by 1H NMR.

In order to find efficient catalyst UMons developed new types of catalysts, which are based on carbene-type catalysts. To reduce the extent of these side-reactions, they developed different types of carbene-based catalysts that are protected with a series of ligand as shown below (see Figure 4 in attachment). Initial trials were done on five-membered carbenes being commercially available.

This rational choice resulted from the fact that the five-membered carbenes (Figure 3) were not thermally stable enough at higher temperatures. Thereby, UMons developed thermally stable 6-membered carbenes for bulk polymerization (see Figure 4 in attachment). The protection of these 6-membered carbenes was again considered to further control the activity of these catalysts. These catalysts were further investigated as efficient catalyst during the latest period of the project.

N-Heterocyclic carbenes (NHCs) are as a part of catalyst designed in the InnoREX framework. Combined with the aforementioned properties, the flexibility with regard to ring-size, N-substituents, and backbone has won NHCs a prominent position in ROP chemistry. With this new type of protected catalysts UMons was able to decrease the extent of epimerization compared to that of earlier organic based catalysts.

Synthesis

The synthesis of the three NHC’s catalyst has been synthesized in the identical way and protected with the choice of the ligands such as CO2, CS2, MgCl2. Among the three of them catalyst 1,3-dimethyl-3,4,5,6-tetrahydro pyrimidin-1-ium-2-MgCl2 (Mg-NHC) proved to be an ideal choice for bulk polymerization of L-Lactide due to its competence.

N,N’-Dimethyl-1,3-propanediamine (5.39 g, 1 eq), ammonium tetrafluoroborate (5.53 g, 1 eq) and trimethylorthoformate (7.00 g, 1.25 eq) were added to a round bottom Flask and heated at 120 °C for two hours under stirring. The mixture was then filtered to yield clear oil. This clear oil was further treated with potassium tertiarybutoxide under nitrogen atmosphere. The resultant mixture was filtered by using cannula and added to magnesium chloride under anhydrous conditions. Upon prolonged stirring under inert atmosphere a precipitate was obtained which upon filtration dried over vacuum as off-white powder.

Towards Lactide ROP via carbene catalyst(s)

To obtain the optimal results the aforementioned three different carbene catalysts (see Figure 4 in attachment) were tested at high temperature (i.e. 170, 190, 210 °C). Among these three catalysts Mg-based N-Heterocyclic carbene Mg-NHC showed the finest possibilities for bulk polymerization. In addition to its low toxicity for biomedical purposes, it has been proposed that the MgCl2 is released upon deprotection and then acts as a co-catalyst in the polymerization, increasing the polymerization rate. UMons synthesised the magnesium protected 6-membered carbene (see Figure 5 in attachment) to test its performance as a catalyst for the ROP of lactide at high temperatures.

As the activity of the carbene-MgCl2 had been verified, a series of polymerizations were then performed to evaluate its kinetic features towards L-lactide (LLA) ROP at various temperatures and different time intervals without any purposely-added initiator (see Table 1 and Figure 6 in attachment).

These results show that the magnesium-protected carbene performs well for the ROP of LA. Additionally, the 1H NMR results showed no sign of epimerization. The highest monomer conversion could be even obtained at 170 °C after 15 min of polymerization time with 1:400 molar ratio of monomer to catalyst. Five-cycle DSC analyses were also carried out to highlight the low extent of epimerization on high molecular weight PLA obtained at 170 °C (see Figure 7 in attachment). Such approach is to determine whether these metal-free catalysts can further promote any side-reactions after different heating treatment.
Interestingly, the crystalline features of high molecular weight PLA are maintained even after 5 cycles, indicating the absence of side-reactions.

A melting temperature of 166.6 °C is noticed, with a melting endotherm of 32.3 J/g. These promising results led us to investigate the synthesis of PLA using a small-scale DSC extrusion compounder at 170 °C under a rotation speed of 75 RPM under a nitrogen flow (Initial molar [L LA]/[carbene-MgCl2] ratio = 400). The L-LA monomer got fed into the DSM machine at 130 °C before increasing the extrusion temperature at 170 °C. The evolution of force recorded with time is reported in Table 2 in the attachment. UMons found out that the force increased with extrusion time, indicating that this carbene-type catalyst was active enough to efficiently promote the continuous synthesis of PLA. This was further supported by molecular characterizations (GPC and 1H NMR techniques) where a monomer conversion of 80% was recorded, together with Mn = 47,200 g/mol and ĐM = 2.00. No significant epimerization is observed by 1H NMR spectroscopy. Again and to support the absence of epimerization, five-cycle DSC analyses were carried out to on the resulting PLA before and after monomer purification (as obtained by solubilization in chloroform and precipitation from MeOH (see Figure 8 in attachment).

These promising results highlight that the carbene-MgCl2 catalyst is still active and efficient towards the synthesis of high molecular weight PLA before any purification step. After monomer purification the purified PLA chains is of semi-crystalline character with a melting temperature of 166.2 °C after five DSC cycle analyses. This purification procedure enables to remove unreacted monomer as well as the traces of catalyst left in the polymerization medium.

Moreover, the inquisitive reactivity of Mg-based catalyst incites us chemo type-variations for better understanding. Therefore UMons investigated the structure activity relation by altering size of ring, substituents over nitrogen in ring and carbene stabilizing ligands types. Our first choices of modifications were on substituents over nitrogen in the ring and ring size. The proposed structures are in figure 9. The synthesis and yields of three analogues of catalyst 2 are more similar as scheme 1. The polymerization of Lactide with all above mentioned variations of Mg-NHC catalysts (see Figure 9 in attachment), resulted epimerization as it is confirmed by 1H NMR. The monomer conversion was reached to moderate rate even after 30 minutes in the absence of the initiator. To further attest these features three-cycle of DSC analyses were carried out for PLA samples obtained at 170 °C after 30 and 60 min, which showed the epimerization observed. These results indicate that the Mg-NHC seems to afford the best efficiency towards the continuous synthesis of PLA.

Exploitable results and Conclusion

UMons developed a new reactive organo magnesium-based six-membered catalyst, which gratified in terms of effective and efficient polymerization pathway for the synthesis of PLA. This catalyst complemented with controlled molecular weights of PLA with relatively low dispersities and high optical purity as obtained in bulk at relatively high polymerization temperatures. Another advantage of our new organo catalyst is efficiency in the continuous polymerization of L-LA as carried out in a microcompounder. Such features enable us to consider this catalyst towards the continuous synthesis of polylactide using reactive extrusion technology developed in the frame of InnoREX project.

Hielscher: Ultrasonic Polymerization

Hielscher’s research work in the InnoREX project was focused on the investigation of the ultrasonic effects on the PLA polymerization and the development of an ultrasonic process equipment that allows for the precise control of the most important process parameters – amplitude, pressure, temperature, and...
retention time – as well as the integration of the ultrasound – before, during and after the extrusion.

Organic catalysts have been shown to efficiently control the polymerization of lactide, but their activity must still be improved to meet industrial standards. Since sonication is well-known for its beneficial effects regarding the initiation and improvement of catalytic reactions, the ultrasonic treatment of various catalyst used for PLA polymerization is a promising field of research. In general, sonication can increase catalyst activity and enable precise control of the reaction by exciting only small parts of the reaction mixture without response time.

In the project, Hielscher tested several ultrasonic flow cells and developed novel reactor systems, where the ultrasonic energy source is introduced into the medium at different process stages. Three alternative energy sources – ultrasound, microwave or laser irradiation – were investigated for their effect to induce the ring-opening polymerization to ensure the high molecular weight polymerization. During the limited residence time in the reactor chamber, the alternative energy sources introduce the required reaction driving impact into an inline flow cell at a highly-targeted level. It is the goal to avoid thereby the use of metal-containing catalysts such as tin (II) 2-ethylhexanoate, which are used in conventional production processes to raise the polymerization rate of the lactones to an acceptable efficient level.

For the InnoREX pilot plant system, the high power ultrasonic processor UIP2000hdT (see Figure 14 in attachment), which is capable to provide 2 kW of ultrasound power, has been integrated. High power ultrasound is well known for its positive effects on chemical reactions, which is the phenomenon of sonochemistry. When high power ultrasonic waves are introduced into a liquid medium, the waves create high-pressure (compression) and low-pressure (rarefaction) cycles resulting in ultrasound cavitation. Cavitation describes “the formation, growth and implosive collapse of bubbles in a liquid. Cavitation collapse produces intense local heating (~5000 K), high pressures (~1000 atm), and enormous heating and cooling rates (>109 K/sec)” such as liquid streaming with liquid jets of ~400 km/h. (K.S. Suslick 1998)

The ultrasonically generated cavitation forces provide kinetic energy, disperse the particles and create radicals supporting the chemical polymerization reaction.

General positive effects of sonication during a polymerization reaction are:
• initiation of polymerization due to sonochemically created radicals (polymerization kinetics)
• acceleration of the polymerization rate narrower poly-dispersities, but higher molecular weight of the polymers
• more homogeneous reaction and hence a lower distribution of chain lengths

Ultrasonically Enhanced Extrusion of PLA

During the InnoREX project, Hielscher developed and investigated the integration of power ultrasonics at several stages during extrusion. The effects of ultrasonics on the polymerization of lactide to PLA in the extrusion process were investigated in regards to ultrasonic process parameters such as ultrasound intensity, amplitude, temperature, pressure, retention time as well as the point of sonication including pre- and post-extrusion sonication.

To investigate the general effects of sonication, sonication trials with a wide spectrum of varying process conditions were performed at lab scale. Thereby, hundreds of samples were produced. This research allowed depicting the influence of power ultrasound on the lactide / catalyst mixture as well as on PLA (see Figure 10 in attachment). Using the automated data recording of the ultrasonic lab device UP200ST, all relevant sonication data were stored in a CSV file so that an exact analysis was possible.

In the next step, Hielscher set up an ultrasonic recirculation system where the ultrasonic process parameters could be changed in a wider range. This bench-top setup could be operated under elevated
pressures up to 10 barg. The effects of sonication to the mixing of lactide and catalyst as well as to the polymerization reaction were investigated. For the mixing of the reactant, a special flow cell insert was used: With the MultiPhaseCavitator insert MPC48, the catalyst was injected via 48 cannulas directly in the ultrasound cavitation zone into the monomer stream (see Figure 13 in attachment).

The final step was the scale-up of the ultrasonic industrial system to the extruder. Power ultrasound can be applied before, during and after extrusion. For each point of the integration of ultrasound, a special setup has been tested.

Pre-Extruder-Sonication: For the sonication before the extruder, the catalyst and monomer are pre-mixed under ultrasonication using the flow cell insert MultiPhaseCavitator MPC48 (see Figure 13 in attachment). The design of the MPC48 allows to inject the catalyst via 48 cannulas into the monomer stream directly before the monomer/catalyst mixture is fed into the extruder. Using the MultiPhaseCavitator MPC48, a very fine-sized, homogeneous monomer/catalyst mixture is obtained, which is important for an optimal polymerization during extrusion.

Ultrasonic Extrusion: For the sonication during extrusion, the ultrasonic transducer and sonotrode are mounted to the extruder block so that the extrusion stream can be sonicated (see Figure 14&15 in attachment). The sonotrode is adapted to high temperatures and pressures in order to ensure a constant high power sonication. By coupling ultrasound waves into the monomer/catalyst stream during reactive extrusion, highly intense shear forces are applied.

Post-Extruder-Sonication: For the sonication behind the extruder, a heatable ultrasonic reactor was built (see Figure 16 in attachment). This reactor can be attached directly to the extruder outlet. The reactor can be heated up to 300 °C to maintain the temperature of the extruded polymer. The pressure in the reactor can be controlled by a back-pressure valve. The post-sonication is applied to improve the final polymerization grade.

Sonication only: Hielscher’s ultrasonic high pressure flow cell reactor can be impinged with pressures up to 140 barg and enables to intensify the cavitative treatment. The ultrasonic setup allows to display the complete polymerization process firstly, by the application of ultrasonically coupled mechanical shear and secondly, by the input of thermal energy.

From the technical standpoint, Hielscher can offer a complete ultrasonic system that can be integrated into any extruder blocks. Both, sonotrodes / ultrasonic horns and ultrasonic reactors are available in different sizes and shapes and capable to perform under high pressure and high temperature conditions.

Modelling

With the goal to display power ultrasound treatments into a model, Hielscher performed a broad range of trials in order to investigate the correlation of amplitude, pressure and temperature. These parameters are required to implement sonication in a numerical software simulation.

The results obtained were used for a regressive analysis. Based on the results of the regression analysis, Hielscher has developed a formula that allows to calculate the ultrasonic surface power output as a function of ultrasonic amplitude, pressure and temperature.

Efficiency and Costs

Efficiency rating: In order to estimate the cost of the sonication procedure, energy input and sonotrode wear have been exactly measured. Since the sonotrode is the only part that is subject to wear and tear and must be replaced after certain time periods depending on the sonication intensity and medium, the average wear has been measured in order to give a profound cost estimation for the ultrasonic extrusion.
Dissemination and Exploitation
Hielscher offers the ultrasonic equipment for the implementation in extrusion lines. Industrial ultrasonic equipment for the sonication during extrusion as well as for the pre- and post-treatment are available systems for clients and customers worldwide. Hielscher supplies the ultrasonic systems in the field of (reactive) extrusion, polymerization and polymer compounding as well as for ultrasonically intensified processes, to material modifications, and sonochemical reactions.
In order to raise interest from the industry, Hielscher was promoting the ultrasonically assisted reactive extrusion on exhibitions and conferences.

Conclusion
During the InnoREX project, profound tests on the ultrasonic effects on the polymerization of monomer to PLA using various catalysts have been undertaken. Ultrasound has both physical and chemical effects on the polymer melt. It has been shown that sonication influences the polymerization reaction due to mechanical, sonochemical and thermal effects. The benefits of sonication include the accelerated polymerization of lactide as well as the polymerization under lower extrusion temperatures and/or lower rotation speed. It has been shown that ultrasonics influences the polymerization of PLA positively due to its non-thermal shear and sonochemical effects.
The equipment for the ultrasonically assisted extrusion polymerization is commercially available and can be adapted to various processes. From the perspective of commercial integration, Hielscher gained profound knowledge of ultrasonic effects on the reactive extrusion polymerization, which allows for recommendation of the suitable ultrasonic equipment, process parameters and implementation. Industrial ultrasonicators, reactors and extruder block adapters are tested and readily available for commercial extrusion processes.

MUEGGE: Development, design and setup of an extruder block for injection of microwave energy
The major task of MUEGGE in InnoREX project was the development, design and setup of an extruder block to be integrated into the lab-scale twin screw extruder at the premises of project coordinator Fraunhofer Institute for Chemical Technology (ICT) for injection of microwave energy. It was expected that addition of microwave energy during reactive extrusion of polylactic acid (PLA) will accelerate the extrusion process and improve the quality of the resulting PLA.
During the development and design phase of the extruder block, MUEGGE designed a CAD model (see Figure 17 in attachment) for high frequency evaluation of microwave injection into the lab-scale twin screw extruder for heating the lactic acid.
The outer diameter of each extrusion line of the CAD model in figure 17 is Da = 18 mm, and the distance between the centers of the two screws is A = 15 mm. At the length of L = 60 mm, the screw thread is removed from the twin screws (not visible in Figure 17 in attachment) for improved coupling of the 5.8 GHz microwave. Both the R 58 rectangular wave guides (light blue color) and the twin screws are made of metal. The enclosure surrounding both the coupling devices and the material to be heated – omitted for the sake of clarity – is made of metal, too. The sealing elements in purple color inhibit the lactic acid in the extruder from penetrating into the small gap between the coupling devices and their metallic housing and for keeping the coupling devices in their position inside the metallic enclosures in order to maintain a uniform distribution of the mechanical pressure applied by the lactic acid inside the extruder on the
coupling devices.

The vertical cross-section in figure 18 in attachment visualizes the transmission path of the microwave, passing the lab-scale twin screw extruder orthogonally to the transporting direction of the lactic acid to be heated. The opposite end of the waveguide is terminated by a shorting plunger for reflection of the fraction of the microwave which has not been absorbed by the lactic acid when passing the twin screw extruder for the first time.

According to the results of simulation of the electrical field strength, there is no direct coupling of the microwave to the twin screws of the extruder made of metal. Furthermore, a homogeneous distribution of the electrical field in the material to be heated is obtained according to the simulation of the distribution of the electrical field strength in the horizontal plane in figure 19 in attachment as well as of the electrical field strength in the vertical plane (see figure 20 in attachment).

According to figure 19, the screw thread of the twin screws is removed at the length of L = 60 mm, resulting in the reduction of the twin screws to their inner diameter of Di = 12 mm. This measure facilitates the coupling of the microwave to the lactic acid around the twin screws.

The corresponding simulation of the distribution of the power density in figure 21 in attachment being equivalent to the microwave energy distribution reveals that the injected 5.8 GHz microwave is almost completely (i.e. by 99%) absorbed by the lactide in the lab-scale twin screw extruder. The microwave energy can be controllably concentrated in the lactic acid to be heated in the 60 mm long area around the twin screws without screw thread.

The spectrum of the microwave power density depicted in figure 21 corresponds to 1 W of injected microwave power. According to simulation, the maximum power density to be achieved in the lactic acid to be heated is 91500 W/m³. When increasing the microwave power injected into the lab-scale twin screw extruder, the rise in the resulting power density is commensurate to the increase in microwave power. Consequently, the maximum achievable power density in the lactic acid is approximately 70 MW/m³ when focusing 750 W of incident microwave power into the lab scale twin screw extruder.

Based on these results for the power density distribution, time-related simulations were performed for calculating the absorption of microwave energy by monomer lactic acid in the lab-scale twin screw extruder and the corresponding temperature profiles. The simulations were focusing on the time frame from powering on the 5.8 GHz microwave until the instant of time when the temperature of the lactic acid passing the extruder block for microwave injection has reached its steady state. These simulations are based on the results of the measurements of the dielectric properties of monomer lactic acid performed by project coordinator Fraunhofer ICT, as the temperature-dependent dielectric loss ε″ of lactic acid directly corresponds to the coupling of the microwave and the equivalent absorption of microwave energy by the lactic acid. Correspondingly, the microwave energy will preferably be absorbed in the sections of the extruder block for microwave injection where the temperature of the lactic acid is maximum at steady state conditions, implying a respectively high dielectric loss ε″.

According to the time-related temperature profiles of the lactic acid in figure 22 in attachment, the maximum temperature increase ΔT in the lactic acid can be found in the center of the extruder block for microwave injection just after powering on the 5.8 GHz microwave. The microwave power applied is 100 W. After 10 s of microwave injection, the peak of maximum power increase is slowly shifting in flow direction of the lactic acid towards the end of the extruder block. Approximately 40 s after powering on the 5.8 GHz microwave, the maximum value of the temperature increase is obtained. Just afterwards, the value of the maximum temperature increase is significantly declining and shows small oscillations. After approximately 70 s, the value of the maximum temperature increase is finally almost constant.
Taking into account the values of the power density in the lactic acid and of the temperature distribution in the individual sections of the extruder block each 4 mm long, the distribution of the injected microwave power at steady state conditions in figure 22 is obtained.

The results in figure 23 in attachment represent the particular space resolved distribution of the microwave power in lactic acid inside the extruder block integrated in the lab-scale twin screw extruder at Fraunhofer ICT at steady state conditions. For monomer materials with different temperature-dependent dielectric loss \( \varepsilon'' \) (i.e. with different coupling of the microwave and equivalent absorption of the microwave energy) as well as for twin screw extruders with different parameters concerning outer diameter \( D_a \) of the extrusion lines, inner diameter \( D_i \) of the twin screws and length \( L \) of the twin screws where they are reduced to their inner diameter \( D_i \) (i.e. where the screw thread is removed), different space resolved distributions of the microwave power at steady state conditions will be obtained.

The results of the space resolved steady-state microwave power distribution inside the extruder block for microwave injection were provided to project partners Sciences Computers Consultants (SCC) and Cranfield University (CrU) for implementing the microwave heating process in their software codes for simulation of the reactive extrusion process of PLA in the lab-scale twin screw extruder at Fraunhofer ICT with additional injection of microwave energy.

Based on the simulations showing optimum results for absorption of microwave energy by the lactic acid passing the extruder block for microwave injection, the final dimensions of the extruder block were determined and all parts of the extruder block constructed and assembled. Figure 24 shows the extruder block and figure 25 the entire microwave injection line including a short piece of R 58 rectangular waveguide, an E/H tuner and a shorting plunger.

In figure 24 in attachment, the short piece of R 58 rectangular waveguide on the left forms the interface between the microwave generator (including magnetron, circulator and water load) and the E/H tuner providing for impedance matching, i.e. for optimized coupling of the 5.8 GHz microwave into the lactic acid inside the extruder block. The shorting plunger at the opposite side of the extruder block (i.e. the microwave component on the right in figure 25 in attachment) is for impedance matching of the part of the incident 5.8 GHz microwave not having been absorbed by the lactic acid after having passed the extruder block for the first time, i.e. reflecting the 5.8 GHz microwave optimally back into the extruder block for generation of a homogeneous electrical field distribution inside the lactic acid. As a consequence, the maximum amount of microwave energy is homogeneously absorbed by the lactic acid inside the extruder block integrated into the lab-scale twin screw extruder at Fraunhofer ICT (see figure 26 in attachment).

Injected microwave energy and throughput of lactic acid were the major parameters varied in the experiments performed by Fraunhofer ICT with the 5.8 GHz microwave injection line integrated into the lab-scale twin screw extruder. When applying high energy settings (high temperature or low throughput of the lactic acid entering the extruder block), additional microwave energy turned out not to be beneficial due to the decreasing molecular weight of the resulting PLA (cf. settings 1-3 in figure 27 in attachment).

Additional microwave energy showed to be beneficial for low energy process parameters (low temperature or high throughput of the lactic acid passing through the extruder block) by increasing the molecular weight of the resulting PLA (see settings 4 and 5 in figure 27 in attachment). Setting 6 in figure 27 in attachment corresponds to the InnoREX standard settings: the molecular weight of the resulting PLA could be increased by approximately 20% due to additional microwave energy injection.

Easy scalability is expected when scaling up from laboratory dimensions in figure 26 in attachment to industrial level by decreasing in parallel the microwave frequency from 5.8 GHz down to the industrially relevant frequencies of 2.45 GHz and even 915 MHz. When respecting the reciprocal relation between the
microwave frequency and the dimensions of the twin screw extruder, i.e. scaling up the extruder dimensions according to the wavelength of the microwave, the results of the simulation on laboratory level by application of 5.8 GHz microwave are almost directly transferrable to the industrial dimensions corresponding to the microwave frequencies of 2.45 GHz and 915 MHz, respectively.

Gneuss: Degassing extruder and online viscometer development
Removing volatiles from low viscosity liquids is a straightforward task. By reducing the pressure in a vessel volatiles simply boil out and can be easily separated from the liquid. In polymer processing a more sophisticated approach is necessary. Due to the high viscosity of polymers gases do not migrate fast enough to the surface and can be separated from the melt. Since polymers often undergo a thermal degradation the processing time cannot be extended to a high level in order to compensate the slow migration rate of volatiles. Moreover, often effects like forming foam makes it difficult to separate the volatiles from the polymer matrix. The transport mechanism can be described in a good approach by diffusion. According to the well-known Fick’s law of diffusion the diffusion rate in a direction $x$ can be approximated by $\frac{\Delta n}{\Delta t} = -D A \frac{dc}{dx}$. Here $n$ is the particle number of the volatile to be removed, $A$ the surface area of the exchange, $c$ the concentration and $D$ a phenomenological constant, depending from e.g. material and temperature conditions. The Gneuss MRS technology boosts the migration of volatiles out of the polymer by two parallel effects. First the polymer is spread over a relatively large area and second a very thin film is formed. This is done by a dynamic process inside the MRS screw system. Therefore the surface of the polymer is renewed with a high rate without adding a too high shear stress to the polymer system, which might lead to degradation and uncontrolled process conditions.
The system works as follows: The MRS processing section is formed like a single screw degassing screw with a length of 2 to 10 screw diameters. In order to achieve high mixing properties, in the main degassing screw up to eight cylindrical shape cavities are incorporated in the main degassing screws. The bore diameter is approximately a quarter of the main screw diameter and these cavities are opened to the degassing area by a quarter of the contour and in the full length of the degassing section. These cavities literally form a barrel of a small degassing extruder and are equipped with degassing screws rotating in counter-direction of the main screw and a speed of approximately 4 times of the main degassing screw. The counter-rotation of the main screw and the incorporated satellite screws allow a folding of the polymer surface with a high rate whereas the shear stress is comparable to standard single screw degassing systems contrary to state of the art mixing technology like co rotation twin screw extruders.
In work package 4 of the InnoREX project these excellent degassing properties of MRS extrusion systems have been made available for the In-line purification of PLA produced in twin screw extruders. Therefore a melt fed MRS system had to be developed (see figure 28 in attachment).
The MRS system is normally configured with a feeding screw at the inlet and a pumping screw at the outlet. In such configuration plastic material can be processed from pellets to melt (for further production) with intermediate de-volatilization. In the InnoREX project a flexible prototype system was developed. This system can be equipped either with a standard feed screw and hopper or in a second configuration as a melt fed system. Contrary to systems in combination with feed screw the filling grade, the rotational speed of the de volatilization unit and therefore residence time and shear stress in the processing unit can be controlled in a wide range. The melt fed system consists of a small (<4D) side feed feed screw. The whole system is driven by the small melt fed screw, which had to be optimized for a sufficient sealing to the drive system of the MRS to avoid leakage. Based on this system the MRS can be fed with pressures (depending on design) of several hundred bars.
The gear system of the MRS was improved during InnoREX with respect to optimized mixing properties and for shear stress adjustment in the single screw satellite units. This allows the future use of such systems in thermal and shear stress sensitive polymers.

During InnoREX a lab scale extrusion system was developed and built, which also allows processing of small throughputs (less than 20 kg/h) under realistic conditions for later scale up. Therefore also for the development of new processes under research conditions MRS systems will be available in the future due to the InnoREX developments. The advantages of the devolatilization technology could be examined and evaluated during the research phase with the lab size technology. Therefore as an important outcome of InnoREX, the MRS technology became available for research projects in process development and as a result the MRS technology can much easier be evaluated for new production technologies.

This MRS-lab system which is described above was successfully integrated to the Fraunhofer ICT lab system with twin screw reactive extrusion process (see figure 29 in attachment) and a combined and complex lab size process including MRS technology could be demonstrated during the InnoREX project.

Development of online characterization system for extruder integrated viscosity measurement

One of the most important parameters to describe the flow characteristics of a plastic melt is the viscosity function. In an extrusion line the value of the viscosity varies mainly with shear rate (due to the common shear thinning behavior of plastic melts) and the temperature and with minor effect at the typical extrusion conditions with pressure. If theses parameters are constant, the viscosity will be determined by material properties (e.g. chain length of polymer molecules, content of fillers) in a pure plastic melt and will be in direct relationship to the physical properties of the material such as tensile strength and impact resistance. In the context of the InnoREX project the viscosity therefore allows an evaluation of polymerization rate and the amount of low molecular weight content (e.g. monomers). Since the reaction is controlled in a twin screw extrusion system the best results with respect to process control are expected, when measuring the viscosity directly inside the extruder barrel.

Gneuss GmbH developed a rheology sensing unit for integration into a twin screw extruder for InnoREX (see figure 30 in attachment). With respect to an easy, straightforward and robust measurement system the following approach for realizing a viscosity measurement was chosen. By means of a high precision metering gear pump, a small part of the polymer melt is separated from the extruder barrel. A pressure of a few bars in the range of 3-10 bars needs to be built up from the extruder in the section, where the measurement takes place.

The body of the measurement unit is similar to a standard section of the extruder barrel and equipped with the necessary melt channels for feeding the viscosity measurement. The polymer is pumped through a precisely manufactured slot capillary. Both the melt temperature and the melt pressure (measurement in 2 positions) are monitored. Figure 30 in attachment shows the design and measurement principle of the developed rheology sensing unit. The rectangular shape of the capillary allows a rheologically optimized design of the capillary in the region of pressure measurements when state of the art pressure sensors for extrusion are used, because they have a flat surface with perfectly fits the membrane of the sensors. If the two pressure measurements for melt pressures P1 and P2 are separated by a distance L for a given volume flow V, the representative viscosity $\eta_{\text{rep}}$ and shear rate $\gamma_{\text{rep}}$ are calculated according to standard formula from the mentioned parameters by the control system attached to the viscosity measurement unit. The depth of the capillary slot is specified according to the material properties within a range of 0.5 to 2.0 mm.

For the capillary a rectangular shape with height $H$ and width $B$ was chosen. This rectangular shape allows
a rheologically optimized design of the capillary in the region of pressure measurements when state of the art pressure sensors for extrusion are used, because they have a flat surface with perfectly fits the membrane of the sensors. If the two pressure measurements for melt pressures $P_1$ and $P_2$ are separated by a distance $L$ for a given Volume flow $V$ the representative viscosity $\eta_{\text{rep}}$ and shear rate $\dot{\gamma}_{\text{rep}}$ are calculated according to standard formula from the mentioned parameters by the control system attached to the viscosity measurement unit. The depth of the capillary slot is specified according to the material properties within a range of 0.5 to 2.0 mm. The body of the unit is designed in cylindrical shape. A gear motor drive is mounted directly to the body of the rheology sensing system. During the demonstration phase of the project the whole mechanical setup was successfully tested with various processing conditions in order to proof the design concept with the PLA line.

Fraunhofer ICT: Project coordinator combining the InnoREX production line
The role of the Fraunhofer ICT within the InnoREX project was, beneath its coordination, to build up the production line and to combine all parts of technologies which have been developed during the project. Such the combination of the project, the continuous, highly precise, polymerization of lactide using alternative energies for reactive extrusion has been realized and performed in the labs of the Fraunhofer ICT.

To achieve this first an understanding of the polymerization within the twin screw extruder was build up. Especially the greatly changing viscosities, from the liquid monomer to a high molecular weight polymer, had to be precisely understood, and respected in terms of extrusion process, screw configuration and extrusion parameters. During the course of this optimization non-literature known extrusion phenomena have been revealed by the researchers in course of the InnoREX project. Especially the resulting residence time proofed to be greatly influenced by different evolution of the material viscosity. Consequently lots of effort has been drawn on the screw configuration development and processing temperature profiles to allow handling the material and the polymerization.

Over the lifetime of the InnoREX project, of course the here generated knowledge is of great basis and influence for any coming extrusion process including demanding material behavior. This covers polymerizations within twin screw extruders of different material systems, not only covering ring opening polymerizations. Of course the here generated knowledge may be further utilized for processes showing the opposite viscosity behavior, such as degradation reactions or viscosity and molecular weight optimizations for example, as often performed for Polypropylene type systems. In the future Fraunhofer ICT will be able to offer partners from industry high sophisticated consultation, including handling of material systems in twin screw extruders, which do highly differ from classical compounding tasks. With hardware supplied by partner Hielscher, Fraunhofer ICT realized the process intensification in twin screw extrusion by means of ultrasound. Using the optimized extruder barrel and sonotrode it could be made sure that large parts of the melt are treated with ultrasound energy. Using the knowledge generated before it could be realized to count for optimal conditions for Ultrasound incorporation under the sonotrode, especially in terms of material viscosity and color (see figure 31 in attachment).

Finally by the researchers of the Fraunhofer ICT it could be realized to intensify the polymerization performance utilizing ultrasound energy. Beneath a beneficial effect on the resulting molecular weight of the produced samples, especially the amount of residual monomer could be considerably lowered for all process settings.

With hardware supplied by partner MUEGGE, Fraunhofer ICT realized the process intensification in twin screw extrusion by means of microwave. Using the newly developed extruder barrel the interaction
between the microwave and the metal housing could be minimized, resulting in a homogenous microwave distribution within the extruder without any sparking or other unwanted side effects. Such microwave energy could be included into standard, metal build extruders without the need of special ceramic components for example. Using this setup microwave energy could be successfully incorporated into the reactive mixtures. Unfortunately no that clear positive conclusions can be drawn from the effect of the microwaves on the here evaluated reaction.

Summing up the incorporation of alternative energies, the researchers could not only show the possibility of their incorporation, but also which material requirements do have to be fulfilled for effective material treatment. During the course of the InnoREX project the influence of both alternative energies has been shown on the polymerization of lactide. In the future of course the energy incorporation into other material systems can and should be investigated. Within InnoREX it was only possible to evaluate the energy incorporation onto the polymerization of PLA, but of course all the broadness of applications performed in extrusion systems may be thought of to be intensified by ultrasound or microwave energy. Efficient heating in food production, efficient molecular mixing in reactive extrusions, shearless energy incorporation for sensitive systems or of course additional energy input for reactive extrusions, curing, reaction initiation or else can be thought of as possible further utilization for the here shown proof of principle, of the straightforward microwave and ultrasound incorporation into twin screw extruders.

With hardware supplied by partner Gneuss, the online recording of the viscosity within the processing length of a twin screw extruder was realized. Using the side stream capillary viscosity technology a direct monitoring of the melt viscosity, and extent of the reaction, became accessible for the researchers. As the online viscometer device can be placed anywhere within the processing length, the viscosity development over the processing length could be monitored. After comparing the online measured viscosity values with offline measured molecular weights, a calibration curve could be produced, allowing evaluating material quality and success of reaction in real time.

Following the argumentation from above, of course getting real time insight into viscosity development of demanding systems is of strategic benefit for research and quality control. As mentioned above viscosity is of vital importance for nearly all materials processed in extrusion technologies. Consequently the here developed technology can and will be utilized for a broad spectrum of tasks. Research questions as process optimization, general process understanding, production optimization or recorded 100% production control from now on can be answered by the researchers with the help of online viscosity (see figure 32 in attachment).

Using hardware, again supplied by project partner Gneuss, an extrusion tandem line could be build up, consisting of a twin screw extruder coupled with a melt fed MRS extruder, while the twin screw counted for effective mixing of the reaction mixture, the MRS device was utilized to remove residual lactide by evaporation and vacuum technology. Depending on the beforehand used reaction conditions it could be shown, that different amounts of residual lactide were present in the MRS extruder. By removing that residual monomer streams out of the melt a purified, high viscosity product exiting the tandem line could be ensured (see figure 33 in attachment).

Additionally all of the here described processes and tasks could be followed using near-infrared (NIR) spectroscopy. Using this analytical method not only measurements at the extrusion die, reflecting final material quality, but also measurements within the processing length of a twin screw extruder could be realized. So it became possible to follow the polymerization reaction over the processing length and to reveal where the different part reactions became dominating and which process changes influenced the polymerization or side reactions. Using this, the researchers could effectively alter process setup and
conditions, without the need for time consuming wet chemical analytics. Also the influence of the above mentioned ultrasound incorporation and microwave incorporation could be followed using NIR spectroscopy (see figure 34 in attachment).

As outlined for the case of online viscosity analytics, real time spectroscopy opens way to a broad number of process optimization and -control options. Far more detailed then observing viscosity, spectroscopical analytics allow a very narrow product control, by beforehand defining spectral conditions to achieve and critical wavelengths thereof. With limited demand for data interpretation this can be translated into a ‘in spec’/’out of spec’ signal for line workers. Avoiding the production of non-saleable lots provides large economic benefit of a close production control utilizing the here displayed spectroscopical methods. Beneath industrial cooperation, the here gained knowledge will be exploited to use it in new research collaborations.

Finally as partly public funded body the here gained knowledge will be exploited in the field of teaching, especially the education of students throughout the professors linked to our institute Prof. Peter Elsner and Prof. Frank Henning. Within their university chairs of polymer technology at the faculty of material sciences and lightweight design at the faculty of vehicle systems technology students will be taught in class but also in practical workshops conducted at the Fraunhofer ICT. Also an exploitation of the results by commercially conducted education of workers in the field is envisaged by Fraunhofer ICT.

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

Comprehensive literature survey and background study to understand the basic principle of ROP process for manufacturing PLA was conducted. The availability of experimental proofs and details in the field of ROP of PLA was useful and formed the basis to develop the understanding of the state-of-the-art. The first task was to understand different stages of ROP process reported in literature with the conventional method, using a metal catalyst.

The details of the project methodology are described as a flow chart in figure 35 in attachment. The reaction rate kinetics for the process was modelled in the form of mathematical differential equations (step 1). The effect of temperature on rate kinetics was then added to this model (step 2).

Step 3 involved the use of Ludovic® software, used for simulation of the extrusion process. The output of kinetic modelling (step 2) in the form of isothermal curves was used to describe the reaction kinetics as an input parameter in Ludovic® simulation software. This in turn also involved using alternative energy as an additional input parameter (in the form of heat) to the Ludovic® simulator. Step 4 & 5 involved repeating the process of kinetic modelling for Ludovic® simulation by adjusting the model to accommodate for the newly developed organic catalyst (OC) along with the use of alternative energies (AE).

Simulation technique

To understand the reaction kinetics and rate equation, it was necessary to perform an intense literature survey of several experimental and theoretical studies. Parameters such as rate constants, activation energy and concentration of reactants are some of the factors that influence the conversion rate of product for any chemical reaction. Tools such as Polymath, Mathematica and MATLAB were considered for the simulation of ROP of PLA. MATLAB was selected based on features like, simple handling of vectors and matrices, easy variable declaration, easy coding and expertise. MATLAB proved to be a prominent method to solve the rate equation and verify the validity of the model with experimental and literature data.
Simulation of most suitable reaction mechanism
The initial trials and case study of reaction mechanism were performed based on literature data. The comparison of theoretically and experimentally reported data showed slight deviation. To overcome the deviation in the results, further literature investigation and modification were conducted. The new finalized reaction mechanism of ROP of Lactide covers side reactions and its effect on reaction output. Effect of temperature in the reaction rates as well as the issues caused at high temperature were simulated and validated with experimental data. The details of the new five stage reaction mechanism can be found in figure 36 in the attachment.

Results of mathematical modelling of ROP process
Based on experimental data provided by research partners (Fraunhofer ICT & UMons), mathematical simulations of most suitable reaction mechanism were performed at different conditions and as output, several isothermal curves considering molecular weight \((M_n)\) versus time (t) and conversion (X) versus time (t) were provided to SCC to be implemented in Ludovic® to perform reactive extrusion simulation.

Generation of Isothermal curves
In order to generate isothermal curves from the batch process, different reaction conditions were considered:
Iso-thermal curves based on the initial conditions of extrusion using the ultrasound source as AE
The isothermal curves, conversion (X) and number average molecular weight \((M_n)\) versus time (t), for total reaction time of 6 min and temperature range of 150-300 °C were 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 Figure 37 in attachment.

Iso-thermal curves based on the initial conditions of extrusion using the microwaves as source of AE
The isothermal curves, conversion (X) and number average molecular weight \((M_n)\) versus time, for total reaction time of 30 min and temperature range of 160-230 °C were 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 Figure 38 in attachment.

Iso-thermal curves based on the initial conditions of batch process experiment using the Mg-Carbene catalyst
The isothermal curves, number average molecular weight \((M_n)\) and conversion (X) versus time, for the total reaction time of 1 hour and temperature range of 150–210 °C were developed to facilitate input for Ludovic® to perform further large scale simulation in future. The duration of the input data was based on the residence time reported from experiments on reactive extrusion of the Lactide. Details of the input data are shown in Figure 39 in attachment.

Conclusion
The initial experimental trials of ROP of lactide in reactive extrusion process shows that the application of AE can improve the performance of the reaction. It was established that the application of ultrasounds and microwave sources boosts the growth of polymer chains.
In addition, the simulation of the batch process was validated through the results obtained experimentally. The mathematical model was implemented in Ludovic® software to simulate and optimize the reactive extrusion process. This was done by implementing isothermal curves for the conversion and number average molecular weight in Ludovic® software.
The result reported through actual experiment and those from the simulation in terms of number average number molecular weight ($M_n$) and conversion $X$ are similar. This work represents a big step forward in the field of modelling of ROP of lactide polymerization. Until now, most of the simulation techniques have been applied on standard processing conditions of polymers. Obviously, the final output from continuous reactive extrusion process could not be predicted as the influence of reaction stages and reaction rate kinetics during the processing stage were not taken into consideration. With InnoREX project, the PLA polymerisation simulation in a TSE has been considered at industrial level. Also, simulation of reaction mechanism considering AE source in the reaction process is a major break-through in this field. The combination of the models developed by Cranfield University, UK and their use in Ludovic® by SCC, France now make it possible to reliably predict the output of the reactive extrusion process of PLA. This process can potentially be extended to any polymer. Thus, this can save time and money required to set up industrial scale production facilities.

The dissemination and exploitation activities of key results and finding of the research effort was done by publishing several open access research articles and presentation in scientific conferences:

Publications:

Workshop and Conferences:
2. Certificate as a speaker @Science for the Green Economy Conference, Cranfield, UK (2015)

SCC: Ludovic-Simulation of microwaves in extrusion process, and integration of kinetics of PLA polymerization
In InnoREX the action of SCC is totally dedicated to the simulation. SCC’s action has been focused on
1. The implementation of µ waves energy into the pre-existing software Ludovic® dedicated to the simulation of the twin screw process
2. The integration of data describing the kinetics of PLA (as described below) as input for the prediction of reactive extrusion
3. The support of compounding simulation for scale up
In this report the description of results and the discussion of their potential impact are discussed separately.
InnoREX results: technical description

Implementation of µ waves energy (in collaboration with MUEGGE):

It has been found that alternative energy sources (laser, ultrasound, and microwave) could be a prominent option to facilitate the ROP of PLA via continuous reactive extrusion. The implementation of metal-free catalyst and suitable application of alternative energy source in the ROP of PLA may result in complete extraction of the metal catalysts and production of considerable amount (30-40) kg/hr of PLA. To replace the participation of metal catalyst, which is a primary factor of toxicity and hazardousness, implementation of metal free catalyst supported by alternative energy proves to be a prominent option.

Microwave setting up:

The microwave device is attached to the barrel in Ludovic®. This specific barrel must have two requirements:
1. No screw element
2. Full filled zone

For achieving the second aspect, a ring element is used in this barrel and a negative conveying element must be mounted after the ring in order to have full filled zone. The Figure 40 in the attachment shows an example of screw configuration (from ICT) with microwave barrel (in green). The microwave provides additional power.

The microwave power is defined into Ludovic by using a power and its distribution:
• with Gaussian form along the microwave device. This example is showed in the Figure 42 in the attachment.
• with an uniform distribution (see Figure 43 in the attachment).
• with a distribution defined by user – provided by MUEGGE (see Figure 44 in the attachment)

Ludovic® simulation:

The microwave effect is taken into account via thermal equilibrium equation, as a third thermal source (the 1st and 2nd terms are viscous dissipation and conduction). The Figure 41 in the attachment shows the contribution of 3 different effects to the variation of temperature. In fact, in microwave zone, no barrel regulation is mounted (conduction effect in blue), also, due to the use of ring, the shear effect is negligible (viscous dissipation is red) and then only micro-wave heating works (microwave effect in green). The heating effect of microwave is not higher than dissipation energy (when comparing the magnitude of green curve and red curve) but thanks to the concentration of energy in a small space and no barrel cooling applied, the increase of temperature is much more important.

It is necessary to analyse the effects of microwave power on Ludovic® modelling. By keeping the same distribution as Figure 42 in the attachment, the microwave power is changed respectively 0; 100 & 250 Watts. The microwave heating and temperature profile for each power level are plotted in Figure 45 in the attachment – temperature on the left axis and microwave heating effect on the right. In this case, all barrel regulation has been removed for a better illustration of microwave power effect on temperature.

Integration of data describing kinetics of PLA

Within Ludovic® the material flow is described as stationary. The history of the material is described from the hopper to the exit as considered as a stationary flow. Thanks to the collaboration with Fraunhofer ICT & Cranfield University (CrU), who provided data describing the kinetics of LA polymerization according
different catalysts. The reaction data are presented via the conversion rate and the molecular weight.

Reaction data as the inputs
ROP of lactide were performed at Fraunhofer ICT lab. The extruders used have diameters of 27 mm and 18 mm. Mathematical modelling and simulation of the complex and detailed reaction mechanism for the ROP of Lactide were considered to model the experimental data provided by ICT. The isothermal curves were developed by CrU to facilitate input for Ludovic®. Comparison of Conversion (X) with time for 6 minutes has been considered. The duration of the input data was based on the residence time reported by ICT for continuous reactive extrusion of PLA. Details of the input data are shown in the Figure 39 in the attachment.

Ludovic® simulation
Since the viscosity changes along the extruder with the reaction progression, it needs to be taken into account into the simulation. This work could be assumed thanks to online viscometer. This device is aimed at measuring the viscosity directly in the extruder. ICT have run an experiment campaign with different ratio LA/PLA (without catalyst, so no reaction occurs during the extrusion). The %LA varies from 0% to 20%, the measurement was realized at 90 s 1 and 190 °C (approximatively). The data are then plotted in the Figure 46 in the attachment. In fact, the viscosity has more or less a stray zone at low %LA before decreases strongly with an increase of %LA. An exponential trend has been found and its fitting is quite good. The later would be very helpful for the understanding of %LA effect on viscosity and subsequently define an analytical coupling between reaction and viscosity.

It needs to be kept in mind that during the extrusion the viscosity follows this curve from the green point to the red one, but viscosity depends not only on %LA but also on the level of molecular weight (as presented in deliverable D5.3).

This work should be concluded with the thermal sensitivity trial of viscosity. Unfortunately, it was impossible due to some technological difficulty of measurement. The alternative solution is to make the assumption about viscosity change by section instead of continuous way:
• Low viscous material: LA rich (beginning of reaction)
• Viscous material: LA medium (middle of screw)
• High viscous material: PLA rich (for the last zone of screw)

The Ludovic® simulation is then set up with 3 products – 2 transition zones (see Figure 47 in the attachment). The reactive extrusion is then performed and the results are plotted in the Figure 48 in the attachment.

Support of compounding simulation
Based on the result in lab scale extruder, the up-scaling work has been performed in collaboration with ICT, AIMPLAS and BHI. This scale up strategy is proposed for both: metal catalyst and organic (InnoREX catalyst).

For the metal catalyst, high temperature and long residence time have good impact on the reaction. However, it is found that for an efficient REX with InnoREX (organic) catalyst, overheating needs to be avoided. The material should be heated up to around 190 °C. The residence time is also a key factor, it is best to maximize this time until 800 s. The scale up is performed with and without alternative energy. Some changes on screw configuration were
also proposed for increasing the REX efficiency. With the use of metal catalyst, the optimum feed rate is 20 kg/h for a rotation speed at 50 rpm (without microwave) and 60 kg/h – 400 rpm (with microwave). The conversion rate and molecular weight are really better with the use of microwave. As far as the organic catalyst, according to the constraint on time and temperature, the optimum feed rate is 20 kg/h for a rotation speed at 400 rpm (without microwave) and 100 rpm (with microwave). In fact, by adding the microwave, the conversion can get a bit higher and the molecular weight remains the same. The advantage of microwave is once again demonstrated, it allows getting higher feed rate. Otherwise the organic catalyst is still challenging for the scale up, the feed rate cannot be higher than 20 kg/h.

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

A Life Cycle Assessment (LCA) study was performed all along the InnoREX project in order to evaluate the potential environmental impacts of polylactide (PLA) products made of PLA produced with InnoREX innovative technologies. The aim of this study was to identify in which process and Life Cycle steps further optimization work would be relevant in order to further diminish the environmental impacts of PLA, as well as to verify whether InnoREX technologies would, as first expected, have the potential to result in PLA products more environment friendly than those made of state-of-the-art (SOA) PLA. LCA tools and methodologies were used in order to model InnoREX PLA and SOA PLA productions. Those models were included in global Life Cycle scenarios, encompassing all the Life Cycle of PLA-based products from the cradle (maize production) to the grave (landfilling). Figure 49 in the attachment shows the global Life Cycle of PLA; the steps InnoREX processes focussed on are highlighted. In the first scenario, a SOA-PLA is produced in the US based on US-grown maize and shipped to Germany where it is transformed into an injection moulded device, that is to be discarded to landfill in Germany after a five years use phase. In a second scenario, PLA is produced in Germany based on Germany-grown maize according to SOA technologies, the following steps of the Life Cycle remaining unchanged compared to scenario 1. In the third scenario, PLA and PLA-based injection moulded device are produced in Germany based on Germany-grown maize according to InnoREX technologies, the use phase and end-of-life treatment remaining unchanged compared to scenarios 1 and 2.

The global potential environmental impacts of these three scenarios were calculated using the ILCD 2011 Midpoint+ set of impact calculation methods; Simapro 8 software was used for modelling and calculations. Though many simplifications were to be made for the modelling of these three scenarios. This was on the one hand due to the fact that transparent and reliable enough data were unfortunately uneasy to obtain for SOA PLA production technologies and on the other hand due to a lack of primary data for InnoREX technologies robust enough for a reliable prediction of the upscaling from demonstrator to industrial scale. Nevertheless, significant trends in the results of environmental impacts calculation were revealed by this LCA study, as illustrated in Figure 50 in the attachment.

It appears clearly from the comparison of the results obtained for scenarios 1 and 2 that an integrated and regionalized production of PLA raw material (maize), PLA itself and PLA-based products should result in a significant improvement of the environmental footprint of PLA, especially for indicators such as climate change, ozone depletion, particulate matter, smog and acidification for which reductions higher than 10% are obtained. The observed differences between the results for these two scenarios mainly arise from the avoidance of transportation steps, but also from differences in US and German electricity mixes and differences in European and US agricultural practices. The comparison of the results between scenarios 2 and 3 shows that specific InnoREX innovations may have a real potential for further improving the environmental footprint of PLA, though to an apparently
smaller extent than the regionalization of all Life Cycle steps. This is due to the fact that the PLA production steps that InnoREX focuses mostly on are not the main contributors to the overall environmental impact of PLA, for which production steps before lactide polymerization (including maize cultivation) are of higher importance than post-lactide steps. However, rather significant improvements seem to be achievable thanks to InnoREX process. The influence of the change of catalytic system on the results is of minor importance (at least as revealed by LCA), and the main driver for impact reductions is the potential of InnoREX process to produce finished or semi-finished products in a one-step process encompassing polymerization and e.g. injection moulding, thus avoiding intermediate process steps such as pelletizing, drying and melting of the PLA after polymerization.

The LCA work performed within InnoREX project therefore confirmed that the pre-supposed environmental benefits brought by InnoREX technologies have indeed the potential to become a significant reality, and that InnoREX technologies could be a promising way to optimize the environmental footprint of PLA. All these results would however have to be further confirmed by deeper and refined evaluation once all the processes will be upscaled at industrial scale.

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

The main role of AIMPLAS has been focused on PLA modifications as well as studying different PLA processing processes.

Firstly, the InnoREX PLA grades from WP3 were characterised in order to study the polymer rheological behaviour and select the best processing technology, the goal was to ensure the PLA compounds viscosity in order to be moulded by injection and extrusion process.

In order to achieve the desired and required PLA properties, it is necessary to modify the PLA polymer with different additives in order to protect the polymer degradation during the processing when the PLA polymer is moulded by extrusion and injection moulding. These different PLA formulations are focused to improve the mechanical properties as impact resistance, HDT, tensile elongation which limits the use of PLA in long term applications, such as packaging, automotive and electronic industries.

An exhaustive previous study based on commercial additives potentially suitable for PLA was carried out in order to improve PLA properties which can be classified in different groups: nucleating agents, chain-extenders, plasticizers, heat resistance additives, impact modifiers, processing aid and long term stabilizer.

As every PLA batch from WP3 had different rheology behaviour and with partial results from the characterisation of the additivation samples in WP6, it has been developed three different additivation strategies.

The compounding extrusion was performed in the traditional co-rotating machine, the different additives were selected in order to obtain material desired properties.

Gravimeter feeders were used to ensure a proper mixture of the materials in the screw.

The processing parameters were adjusted in order to avoid the thermal degradation, dispersion influence, screw design and speed, barrel temperature and output, torque and pressure.

The residual lactide content in the material is an important parameter to be considered. Its influence was studied, because the de-polymerisation could occur during extrusion or injection process if there is some lactide content in the final PLA compound.

When afforded the extrusion PLA film manufacture, a study was needed to establish the best processing parameters to improve film PLA properties: melting and rolls temperatures and speed extrusion. After
processing there were mechanically and thermally characterized, in order to ensure the requested properties. The melting temperature of the InnoREX compound is lower in comparison to compared commercial PLA. Because of that, the energy consumption during InnoREX PLA processing versus commercial PLA will be lower and as consequence, allowing energy saving. According to the extrusion trials, it was observed that it was not possible to obtain sheets with high crystallinity even if high calender temperature was set up. Commercial PLA sheet presents a higher crystallinity as InnoREX PLA sheets. Mechanical properties of InnoREX compound indicates that the material developed is more flexible compared to commercial PLA. Moreover, glass transition temperature (Tg) is much lower compared to commercial PLA grades. These results are very interesting for medical applications. Because the additivation strategy was more focused to improve impact resistance on PLA polymer, InnoREX PLA shows an improved impact resistance compared to commercial PLA.

After the extrusion process, using the produced PLA sheets and a semi-automatic thermoforming machine, a final thermoformed PLA package has been produced in order to verify the process viability. InnoREX PLA could be processed by conventional extrusion line and discontinuous thermoforming equipment and this kind of PLA is more suitable for products with 700 µm than 300 µm of thickness. The last trial was done in order to get a thinner film (55-60 µm) for the lids of the trays.

Thermoforming trials were done with the sheets obtained in the previous steps:
1. Pilot plant discontinuous thermoforming equipment (Figure 55 in the attachment) was used for the trials.
2. Figure 56 in the attachment shows the main steps of the thermoforming process and the final trays obtained.
3. The extruded and injected packages have been characterized as product validation using the suitable EN-ISO standards according requirements defined, as can be seen in figure 57 in the attachment.

In order to study sealing processability of the InnoREX sheet/film and later on to characterize pealing test and to study modified atmosphere properties, the different packages have been sealed with the same produced film as material package and introduced a nitrogen flow into the package. The final thermoformed packages have been characterized showing that InnoREX PLA present better peeling properties as mechanical behaviour under cooled conditions than commercial PLA.

Another additivated PLA compound was studied for injection moulding, the best injection parameters (melt temperature, Injection speed and mould temperature) were set according to thermal and mechanical properties obtained. As well as the additivation strategy was studied in order to improve impact resistance on InnoREX PLA, the characterised injected PLA test bar showed an important impact improvement. Flexural strength on injected test bars is influenced with melt temperature and Heat Deflection Temperature with mould temperature. About thermal properties, with mould temperature on InnoREX PLA showed a 60% of HDT increment. The crystallinity has improved a good deal in this grade of developed PLA as with higher mould temperature.

Related to scaling-up studies, in collaboration with BHI and SCC, PLA polymerisation step and compounding extrusion (Figure 54 in the attachment) has been studied in order to show up-scaling possibilities. For that purpose, Ludovic software has been employed for helping to predict different processing conditions (speed of screw rotation and throughput) that result in similar response values than obtained at pilot plant level in terms of energy mix and mean residence time, which are two critical parameters in reactive extrusion reactions.

Exploitable results
In principle, there are two main results allocated to AIMPLAS, which are: Knowledge/ injection moulding process for PLA applications and PLA formulation, the exploitation strategy is defined according to this results:

Knowledge/ injection moulding process for PLA applications
The result will be used for further internal research projects or even consortium projects, where AIMPLAS roles will be mainly to assists the companies and ensure a technology transfer.
In the particular case of InnoREX, it was used for packaging products, even if the packaging sector is the most common for this type of material, in the market there could appear several PLA products for other sectors, which the foreground acquired can be also applied. The key parameters for injections for the injection process as identified in InnoREX have been mould temperature, melting temperature of the material and injection speed.
AIMPLAS can use its background and foreground from InnoREX project for technical assistance to injection companies, helping them with the PLA injection in their machines.

Formulation: PLA additivation
The result refers to the suitable methodology to obtain the final compound, taking into account the several steps to formulate the virgin polymer with several additives that will improve the melt processing of the polymers. The main objective of the formulation of PLA developed in the project is to improve the processability and optimize required properties of the polymer.
The result will be used for further internal research projects or even consortium projects, where a technology transfer can be ensure. In addition several exploitation agreements will be arranged for example with PLA producers, who can be potentially interested in the formulation.

Talleres Pohuer: New PLA grades and case studies thereof mainly focus on manufacturing processes injection moulding.
In InnoREX Talleres Pohuer was leader of the work package demonstrating that the developed PLA grades are possible to be scaled up at pilot plant level. Main topics were the definition and performing of two case studies defined by IEB, and also the definition and development based on packaging requirements. To make this demonstration, Talleres Pohuer used a mould for packaging, which was modified to InnoREX, because the mould was designed for PP moulding and InnoREX material is the PLA. The two different case studies were defined taking into account the IEB companies requirements, aspects as benchmark materials, general strategy, niche markets or end InnoREX PLA properties were considered.
The cases were the following:
1. PLA reactive extrusion production process.- the aim is to replace the current PLA by InnoREX PLA using the same extrusion production process. Productivity, economical study, energy impact and LCA were analysed.
2. Modification of commercial PLA to obtain branching using InnoREX equipment (same optimization equipment as the used for developed InnoREX PLA polymer) to obtain a better branching chain PLA polymer.

In order to select the more appropriated mould from Talleres Pohuer to develop the packaging case study, a survey was circulated between Pohuer´s customers and AIMPLAS´ associates in order to define the packaging requirements. As result of this incoming feedback, final characterization of the injected package was defined as the study of cooling conditions, peeling properties, recyclability or the use of...
modified atmosphere.

As problems occurred regarding the extraction angle for product demoulding, thickness modification of the product base, and with the gasses extraction during the PLA injection, Talleres Pohuer modified a PP package mould to carry out the trials. All problems could be resolved by a series of modifications to the mould.

Based on injection studies performed by AIMPLAS, Talleres Pohuer studied PLA grades which all of them are injectable: the two commercial injection grades (7001D and 3251 from NATUREWORKS) and the InnoREX injection grade PLA. 7001D was injectable at less temperature, less pressure and less speed. Compared to the 7001D grade 3251 is transparent. Different PLA packages were produced to be final characterized in AIMPLAS laboratories as defined in previous survey.

As work package leader, different task results were coordinated. The completed polymerization line holding alternative energy input, degassing device and online analytics, based at Fraunhofer ICT premises and results from WP3, WP4 and WP5, was used to evaluate InnoREX concept and in terms of up-scaling the extrusion line located at BHI was used. The simulation software Ludovic® was used to study the scale-up strategies.

At pilot plant level, the extrusion process and forthcoming thermoforming process was studied in order to obtain a final package.

A final characterization of all injected and thermoformed packages were done in order to compare InnoREX and commercial PLA packages.

BHI – PLA industrial up-scaling

The main objective of the formulation of PLA developed in the project is to improve the processability and optimize required properties of the polymer. The result refers to the suitable methodology to obtain the final compound, taking into account the several steps to formulate the virgin polymer with several additives that will improve the melt processing of the polymers. All the selected and used additives are bio-based, therefore the biodegradation could be ensured.

Scale-up studies:
In order to guarantee the same properties than the polymer (synthesis PLA at Fraunhofer ICT facilities) and compounds (additivated PLA at AIMPLAS pilot plant) a study of scalability has been carried out in order to stabilize the processing conditions for higher scale taking in account that similar response values give the same properties.

For better understanding cooperation between AIMPLAS and BHI due to compounding process scaling-up see figure 59 of the attachment.

In the following the necessary steps to perform the scale up are described.

STEP 1: At first the work methodology (also see figure 59 of the attachment) needed to be defined:
AIMPLAS / BHI prepared data for simulation the production parameters on Ludovic software.

Screw configuration
- Temperature
- Production
- Screw speed

STEP 2: BHI simulation: Current screw
Alphatec S65, Diameter 63.1 mm, L/D 40
DOE results inputs: Flow rate (50-300 kg/h), rotation speed (100-350 rpm). Results see in Figure 60 in the
STEP 3: BHI Simulation: Modified screw
Alphatec S65, Diameter 63.1 mm
Aimplas and BHI were utilizing Ludovic software to identify final process parameters for compounding process of new grade PLA compound.

STEP 4: Compounding process of injection grade of the commercial PLA
Based on identified final production parameters coming from Ludovic simulation, BHI reconfigured the compounder in his production plant (especially the screw configuration and process data) according to the compounding process for the production of the injection grade PLA.
The produced compound was sent to AIMPLAS and TAPO for the preparation of injection moulded containers.

Development of a PLA extrusion and injection samples
Extrusion studies with commercial and InnoREX PLA
Extrusion studies with commercial PLA (additive 7001D PLA by BHI) see in Figure 62 in the attachment.
Different extrusion trials were performed in order to:
- Analyse the extrusion processability of the compound and optimize the extrusion conditions to obtain a sheet of 300 µm suitable for tray thermoforming.
- Check the effect of the cooling rate in the thermal and mechanical properties of the sheet. To do that, different sheets were obtained by using different roll temperatures (35 ºC, 50 ºC and 60 ºC).
- Check the effect in the stretching ratio of the sheet in the thermal and mechanical properties of the sheet. To do that, sheets were obtained at two different calender speeds (2.5 and 4.2).

RESULTS from Extrusion studies with commercial PLA (additive 7001D PLA by BHI)
- Four different samples were selected for further characterization. These are M2, M3, M4 and M5 samples (with different extrusion process settings).
- The best extrusion processability was observed when melt temperature was 160 ºC. The viscosity at these conditions was suitable to feed the die and to obtain a sheet of 300 µm.
- The best aspect and surface of the sheet is achieved when the temperature of the rolls is between 50-60 ºC.

Conclusions:
Formulation of PLA compound for mould injection and extrusion developed in the project can be commercialised by BH Industries. BHI wants to start a production of one or two compounds based on the formulation found and evaluated in InnoREX:
- one for mould injection (potential customer TAPO and other producers of injection moulding details)
- second for extrusion – compound for filament production, for 3D printers

According to market needs, potential interested producers, BHI can prepare some exploitation agreement with PLA compound producers.
Formulation development for PLA additivation and process to modify commercial polymer grades will be useful for preparing new compounds formulation according potential customer needs.
BHI will prepare information about the new PLA compounds for potential client (it will be disseminated on website, on industry exhibitions and conferences).
Potential Impact:

Gained project results and their impact and exploitation by the partners affected:

Fraunhofer ICT developed in InnoREX several extrusion process characteristics to realise the synthesis of PLA from lactide within a twin screw extruder under the incorporation of alternative energy sources. Combining this generated foreground with the adaption of ultrasound energy into the process Fraunhofer ICT realised the process intensification in twin screw extrusion by means of ultrasound, and the process stable incorporation of microwave energy into the polymerization. The here gained knowledge will serve as basis for future projects and collaborations. Further the here gained process know how will serve as a basis to be translated to alternative systems in the field of polymerizations in twin screw extruders, but also to (commercially available) material modification, intensified by utilization of alternative energies in twin screw extruders. The here gained knowledge will be exploited in new research collaborations. Finally as partly public funded body the here gained knowledge will be exploited in the field of teaching, especially the education of students throughout the professors linked to our institute Prof. Peter Elsner and Prof. Frank Henning. Within their university chairs of polymer technology at the faculty of material sciences and lightweight design at the faculty of vehicle systems technology students will be taught in class but also in practical workshops conducted at the Fraunhofer ICT.

The role of MUEGGE in InnoREX project was to provide microwave energy for improved synthesis of polylactide (PLA) inside a twin screw extruder. Therefore, MUEGGE developed, designed and set up an extruder block for injection of 5.8 GHz microwave into the PLA material inside the lab-scale twin-screw extruder at Fraunhofer ICT that is easily to be scaled up to industrial applications, then requiring 2.45 GHz or even 915 MHz microwave technology. The extruder block is a modular part and can be implemented into the lab-scale twin screw extruder at different positions.

Hielscher Ultrasonics has developed several methods for incorporation of ultrasonics into the polymerization process of PLA, namely the pre-extrusion (sonication directly before extrusion), during extrusion and post-extrusion. To have optimal control over the sonication process, Hielscher has developed several setup possibilities including the injection of catalyst via „MPC48“ reactor (with 48 cannulas for fine-size injection of the second phase into the ultrasound cavitation zone), high-pressure ultrasonic reactor (up to 100 barg) and the heatable post-extruder reactor. Hielscher Ultrasonics developed a model to calculate the ultrasonic power coupling for various pressures and amplitudes. The model is based on a non-linear multiple parameter model / regression analysis (model fitting via evolutionary algorithm to minimize the sum up of squared residuals).

During the InnoREX project Gneuss developed a lab-size melt fed MRS system for PLA degassing and purification. Before the project, the MRS system was always connected with a feed screw for plastification. This restricted the MRS system to a specific ratio between rotational speed of the degassing system and the mass flow. As an outcome of this project Gneuss gained the knowledge of connecting such system directly to a melt flow. Due to the fact, that the MRS section could be controlled by speed and therefore filling rate and degassing rate independent from mass flow and directly connected to a melt source, new fields of applications were opened to the use of the MRS-technology. Apart from the melt feeding the MRS satellite screw system and the drive for this system could be improved. This had direct positive impact on the lifetime of the drive and Gneuss could observe a doubling of lifetime, therefore large cost savings for customers in MRS technology and of course a higher production efficiency. This strengthens the position of the MRS in the market, which Gneuss already serves.

In work package 5 of the project an online viscosity measurement within the twin screw extruder was
developed by Gneuss. The system is based mechanically on an extruder barrel of the specific extrusion system which has to be equipped with such a measurement. During the InnoREX project a lab scale prototype could be built successfully and the technology could be demonstrated successfully. Nevertheless the system is already interesting to use in research applications and for customers, who are able to determine their own correlation for processing control. Therefore it is planned to offer and introduce such system in a first exploitation phase directly to research laboratories which are contacted anyway during the ongoing sales activities of the Gneuss Sales network.

SCC was involved in the InnoREX project as WP leader for simulation topic. They were in charge in simulating the polymerization and alternative energy input thanks to the Ludovic® software. The results will support the optimization scale-up of PLA reactive extrusion and compounding. The Ludovic® software is completely dedicated to co-rotating twin screw extrusion, taking into account complex thermo-mechanical behaviour for polymer viscosity as well as the polymer reaction. Their key exploitable result consists in the implementation of the alternative source of energy (the microwave) and the ring-opening reaction model of PLA into the software. The alternative energy is integrated as additional source in thermal balance equation and the ring-opening reaction (data provided by Cranfield University), is added into reaction model database of Ludovic®. These evolutions help SCC broadening the abilities of the software. They are the answer for modelling an innovative process. Beyond the usefulness of the microwave option, this demonstrates the capabilities of Ludovic® to simulate such kind of energy. Therefore, SCC increases the accuracy and the level of prediction using the software and enlarges its application area toward the innovative green material and process market.

For University of Mons there is a perceiving demand of metal-free catalyst development for the bulk polymerization of L-lactide in a controlled manner. For the last decades, metal-free catalysts for ring-opening polymerization (ROP) of cyclic esters, such as L-lactide, had a momentum to develop them in solution and in bulk. While many organic catalysts have efficiently promoted the ROP of lactide in solution, there have been relatively few examples that are capable of doing so under solvent-free conditions (bulk) and at high polymerization temperatures (higher than 150°C). The major issues about these catalysts under these conditions are their propensity to promoting inter- and intramolecular transesterification reactions and epimerization. UMons addressed this challenge and prepared an eco-friendly catalyst based on carbene for controlled ROP of lactide that could be efficient at high temperature (up to 190°C). It resulted in a PLA of high molecular weights and high optical purity. Some extrusion trials confirmed the efficiency of this catalyst towards the continuous polymerization of L-LA as carried out in a microcompounder. Such features enable us to consider this catalyst towards the continuous synthesis of polylactide using reactive extrusion technology developed in the frame of InnoREX project. In addition to the increased knowledge for UMons (in terms of peer-reviewed manuscript, etc.), the environmental friendly aspects gives them additional industrial outcome. Post-processing technology for their organocatalyst for bulk polymerization of lactide at high conversion rate, additionally increased UMons’ exploitable result.

To ensure short market entry times of the outcomes of the InnoREX project an industrial exploitation board (IEB) consisting of potential industrial end-users has been established. The members of the board have been invited by the project consortium to take part in workshops and/or informative meetings 1-2 times a year. Here the latest project results have been presented and the members of the industrial exploitation board had the chance to give the consortium a feedback about the strategic development of the project. The IEB was giving additional advice to the project partners with respect to the requirement definition within their sectorial scope, the material and product validation, and the dissemination and exploitation of
Dissemination activities assisting exploitation of the projects results: All the InnoREX partners were involved in dissemination. The dissemination is coordinated by ASSOCOMAPLAST that lead the work package and represent the main contributor to this. One of the important aspects of this type of research project is to ensure that knowledge generated, that will benefit the EU/international science community and plastics industry, is made widely available both in a scientific contribution form - like peer-reviewed publications or participation in scientific events - and in a user-friendly, clear and understandable way for the plastics industry. To assist the mentioned aim, one of the roles of the research partners has been firstly to consolidate the raw scientific findings in order to be inserted into a format that can be most readily assimilated both by the scientific and general community. With the support of the RTD partners and SMEs one, the InnoREX consortium produced basic material (flyers, posters, InnoREX newsletter, InnoREX generic power-point presentation), that have been used as the main sources of dissemination material, together with more detailed scientific papers to be shared with the scientific ad academic community. Evaluating the flyers, posters and newsletters developed in the course of the project life, the content of the dissemination material followed the developments of the research without sharing sensitive information, but aimed to stimulate a commercial interest and facilitate possible business cooperation or request of consultancy from the public. Additionally, dissemination addressed to scientific community has been set in order to go deeply into technical details with a specific academic approach. Moreover, the InnoREX partners’ dissemination activities had to balance the need of letting the scientific community benefit from the research results with the rights of the InnoREX partners to avoid the risk of IPR infringement. Besides sharing the InnoREX results with the scientific community for the present and for future research activities, an important task during the project life has been to focus the promotional activity on the potentially interested parties, especially SMEs in order to stimulate future cooperation with the InnoREX partners in the form of consultancy or business agreement. Considering that InnoREX consortium aims to identify an innovative way to produce and process bioplastics like PLA using alternative energies, part of the industrial sectors to be reached by the InnoREX dissemination has been selected accordingly. One of the plastics sector identified has been the plastics processing technology producers’ sector. To this purpose, participation in international trade exhibitions has been inserted in the plan for the promotion of the InnoREX project to make aware the plastics machinery constructors about InnoREX. During the research period InnoREX project was present in more than 30 international plastics trade exhibitions. In order to reach a wider audience also technical and promotional articles have been published on specific plastics magazines circulated during the mentioned plastics trade exhibitions events. Furthermore, as the bio-based approach has been an important aspect of InnoREX research, also raw material producer and plastics processors operating in the bio-based sector have been targeted. To this purpose, together with the mentioned participation in plastics international exhibitions, promotional activities have been focused on seminars, conferences and events related to bio-based plastics material development. Additional promotional dissemination has been carried out focusing on articles published on national and international plastics magazines, plastics portals and thematic websites. The main project website at http://www.InnoREX.eu/ went live within the first three months of the project and is one of the primary interfaces for dissemination. The public part of the website is updated on a
regular basis, as information regarding events and technical developments related to the project became available. The website will still be available two years after the end of the project.

Several presentations have been used in public events in order to show the InnoREX progress. All the presentations are available to be downloaded from the InnoREX web site and can be used by each partner to promote the research.

As far as dissemination during international trade exhibitions is concerned, promotional activities aimed to stimulate and to keep alive the interest about InnoREX research, highlighting the project goals and expected/achieved results. InnoREX publicity brochures have been distributed during the fairs. Information about the project was shared with interested visitors. InnoREX posters were applied on the wall of the stand. Furthermore, articles about InnoREX project were published on MACPLAS and MACPLAS INTERNATIONAL or local magazine such as TWORZYWA Poland magazine and distributed during the events. Roughly, 3000 copies (5000 in case of the bigger events) of the mentioned magazines were circulated each time.

To summarise the research outputs to date, 5 journal papers have been submitted. Following is a list of published work and potential future publications:

The first two publications were used to disseminate the simulation of a reactive extrusion process, which can now be used by researchers in the field to simulate and optimize the extrusion process in greater detail, enabling further lines of investigation considering process optimization.


The third paper was used to disseminate the results of a study of the state of the art, to the research community. This paper describes the fact that the majority of research has only considered metal-based catalyst and therefore highlights the gap in the knowledge concerning the behaviour of non-metallic catalyst. This paper will help future researchers in this field to gain a broad understanding of the current state of the art.


The fourth and fifth journal publications shared the results of a study investigating the performance of alternative energy sources using microwave and ultrasound techniques. Ultrasound was found to be the most effective method and the application techniques were described within the papers.


The final paper which is currently in progress, with an expected publication date towards the end of 2016,
disseminates the findings associated with the use of an eco-friendly catalyst. Whilst some of the results are very encouraging at a lab scale, the work did not entirely yield expected results, and therefore this paper will also form a very useful basis for further research, which will be required to enable application of the catalyst on an industrial scale.


The project research was also presented at three international conferences in the UK, France and Belgium to further disseminate the findings described above.

The three conference papers were:

2. Oral presentation at “Science for the Green Economy Conference”, February 2016 (Cranfield, UK)
3. Poster and oral presentation at EU funded “Projects-Industrial Workshop”, March 2016 (Brussels, Belgium)

Gender dimension of InnoREX project:

InnoREX had no gender dimension as such in terms of that the research on extrusion, polymerization or alternative energies would have been influenced by gender, as people were not focus of the research. Nevertheless the consortium performed some actions related to gender balance in the project. It is to say, that more than one third of the employees working on the project are female (see Figure 63 in attachment). Also it is worth knowing that the majority (86%) of females involved in the project worked in academia. Figure 64 in attachment shows, that “other employees” form the majority of this group followed by experienced female researchers.

This could be achieved, as mainly the RTD-partners performed gender equality actions as implementing an equal opportunity policy, setting targets to achieve a gender balance in the workforce, or actions to improve work-life balance. Those actions were evaluated effective to very effective.

On the aspect of science education the industrial partners were leading in involving students, school pupils etc. Gneuss, MUEGGE and TaPo, but also Fraunhofer ICT or UMons offered an open house day, girl’s/boy’s days or similar. Involving pupils in research will also help to increase the number of women employed in research in general and also becoming a researcher.

List of Websites:

website: www.innorex.eu
contat details of coordinator: Bjoern Bergmann, bjoern.bergmann@ict.fraunhofer.de phone +49 721 4640-423

Related documents

![related-docs](final1-attachment-holding-figures-and-tables-to-final-report-summary-innorex-2016-07-25.pdf)