A circular multilayer plastic approach for value retention of end-of life multilayers films

D4.6: Publishable report on physical recycling of ML films

WP4: Physical recycling

Project Information

Grant Agreement n°	101003864
Dates	1st June 2021 – 31st May 2024

Document status

Document information

Deliverable name	**D4.6 Publishable report on physical recycling of ML films**
Responsible beneficiary	TNO
Contributing beneficiaries	L. Prins, A. Kalkman/TNO
Contractual delivery date	M40
Actual delivery date	M40
Dissemination level	Public

Document approval

Name	Position in project	Organisation	Date	Visa
C. Chevallier	Coordinator	IPC	30/09/24	

Document history

Version	Date	Modifications	Authors
V0.1	07/10/21	Document created	M. Perrodin
V0.2	04/07/24	Basic content put in	L. Prins
V0.3	22/08/24	Input detailed	L. Prins
V0.4	28/08/24	Review Typo, style, comment	A. van de Runstraat, A. Kalkman
V0.5	23/09/24	Review by Dissemination Board	L. Prins
Revised _CC_LP		Review comments processed	L. Prins
VF	24/09/24	Final Review	C. Chevallier

Table of content

Abbreviations

Abbreviated term	Definition
Al or Alu	Aluminium
Complex	Complex within the CIMPA framework is referring to multilayers that cannot mechanically be recycled and therefore will be processed physically using the TNO Möbius dissolution process. In this Deliverable these terms are all used.
D	Deliverable
DSC-OIT	Differential Scanning Calorimetry - Oxidation Induction Time
Fe	Iron
FTIR	Fourier Transform InfraRed (spectroscopy)
GA	Grant Agreement or General Assembly
HDPE	High Density Polyethylene
Hg	Mercury
LDPE	Low Density Polyethene
ML or ml	Multilayer
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PFD	Process Flow Diagram
PO	Polyolefins, i.e. PE and PP
PP	Polypropene
TGA	Thermogravimetric Analysis
Ti	Titanium
TRL	Technology Readiness Level
WP	Work Package
wt%	percentage by weight
XRF	X-Ray Fluorescence (spectroscopy)

Executive summary

The objective of CIMPA is to develop the first recycling value chain for post-industrial and post-consumer multilayer films retaining up to 72% of their value yield vs 2% actually, based on a synergetic approach combining innovative compositional sorting, mechanical and physical (dissolution) recycling, and upgrading solutions (decontamination, properties improvement, in-line adaptive process control with soft computing feedback loop for stable recycled materials properties).

The Work Package 4 aims at recovery of polyolefins (PO) from sorted multilayer materials that are too complex to be mechanically recycled. Especially metallised foils were identified in the early stage of the project as the multilayers to work on. The technology used is named physical recycling and is based on dissolution/precipitation under superheated conditions combined with removal of impurities and additives between the dissolution and precipitation steps.

This deliverable D4.6 presents the final report on experiments performed at TRL5 scale by chronological description of how the plant was built and how the tests were performed, including the challenges that appeared during the scale-up. It concludes with a presentation of mass balances and a closer analytical investigation into the recovered PO.

The CIMPA dissolution process has shown to have the potential to process kg scale sorted waste sample comprised of complex multilayers (i.e. metallised films) and to recover PO and their separation from other non-PO materials. The recycled PO contained no residual solvent and showed high purity with only a low amount of residual impurities. Obtaining such recycled material is considered a success and lays groundwork for further scale-up and commercialization.

The CIMPA process was executed in a purposely built CIMPA pilot plant with a capacity of 1 kg waste per batch, fulfilling the requirements of TRL5 operation but not reaching yet the desired yields. The lessons learned during the scale-up process of CIMPA and commissioning of the CIMPA plant will be applied to the commissioning of the TNO TRL5 pilot (TNO Möbius Leto[1]) which is planned for Q4 2024.

Deliverable report

Introduction

The CIMPA developments offer a realistic solution to a specific plastic waste consisting in multilayer films, the main added-values of the project for the EU are: (i) up-scalable solutions for significant reduction of plastic waste and reduction of virgin material use and (ii) demonstration that multilayer films can be circular in two large volume segments: food and agriculture.

[1] Recycling plastics through dissolution | TNO

Work package 4 of the CIMPA project focusses on developing a physical (dissolution) recycling process to recover polyolefins (PO) from multilayer waste streams. The recovered PO are intended to meet food contact requirements. PO are recovered selectively from the other layers in the 'complex' multilayer material, whereas the potential for the recycling of recovered fractions of those non-dissolved other polymers / barrier materials (e.g., PET, PA, Al foil) will be evaluated as well.

The knowledge and experience gained in the task 4.1 (Lab scale recovery of polyolefins from complex multilayers) were used in D4.2 for a general description, specifications, and PFD (process flow diagram) of the TRL5 set-up that TNO has built. This design was further developed, including an elaborate safety study.

This document describes CIMPA Deliverable 4.6, titled: *Publishable report on physical recycling of ML films*, and is part of the Task 4.4, titled: *TRL5 scale-up and demonstration of the developed dissolution process for recovery of polyolefins*, of the Work Package 4, funded by the EU Horizon 2020 Programme under the Grant Agreement number 101003864.

After a short introduction on the lab scale results to recap the processing concept, this report will explain the TRL5 set-up with each of the three sub-processing steps, then explain experiments performed during the pilot commissioning and main processing campaign and finally conclude by showing mass balances, and removal efficiency results of recovered PO.

Description

Scale-up of physical recycling technology from TRL3-4 to TRL5

Throughout the WP4, the development of physical recycling based on the TNO Möbius dissolution technology for recovery of PO from complex multilayer materials has been demonstrated.

Earlier in the project, a solvent screening for the selection of a suitable solvent and proof-of-principle experiments with model materials were executed. Next, this was extended to experiments with a real waste which showed that the process developed at lab scale (up to TRL4) can process waste plastic and recover the target polymer (*i.e.* mixed polyolefins in CIMPA) from metallized foils, remove colourants, impurities and other non-PO materials. The set-ups used for the development of the TNO Möbius dissolution process at lab scale (up to TRL4) are shown in Figure 1.

Figure 1 Installations used at TNO for the physical recycling process development. Left: TNO Möbius Hera set-up (TRL3). Right: TNO Möbius Metis set-up (TRL4).

The processing steps are:

1. Dissolution (and coarse filtration)
2. Fine filtration
3. Polymer precipitation and recovery

This processing scheme is shown in Figure 2 as performed on sorted complex multilayer waste.

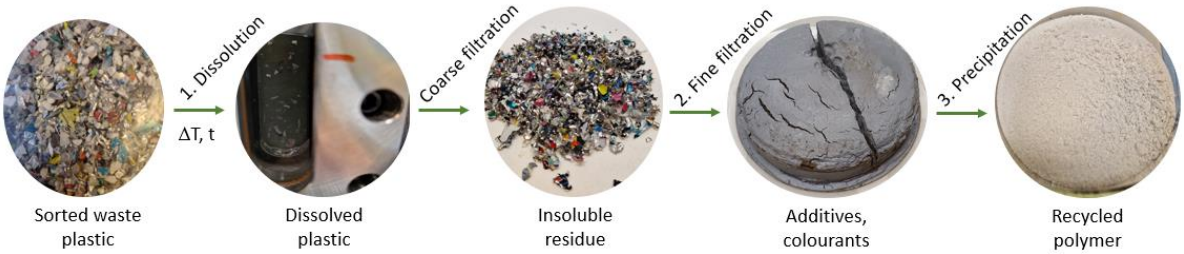

Figure 2 CIMPA processing scheme on sorted waste sample at lab scale.

The recycled PO material from real waste sample was analysed by complementary analytical techniques available at TNO and VTT (such as FTIR, XRF, TGA, DSC) in order to determine the quality of the product and the amount of solvents remaining after the dissolution process of TNO. Thermal analysis of the product confirmed a removal of stabilizers that will need to be added before the recompounding step. No residual solvent was detected in the recycled product confirming that a devolatilization step is not necessary after physical recycling process and the recovered material can be directly upgraded. Furthermore, the recyclate showed high PO purity with a low amount of residual impurities (such as *e.g.*, Ti which comes from TiO_2 added to the foils typically in high quantities to make them white or intensely coloured).

Process flow of the TRL5 prototype for physical recycling

In order to scale up the TNO's TRL3-4 technology for dissolution and realise a TRL5 laboratory pilot scale facility with the capacity to produce kg scale batches of recovered PO after dissolution, a PFD of the TR5 pilot was drawn (see Figure 3).

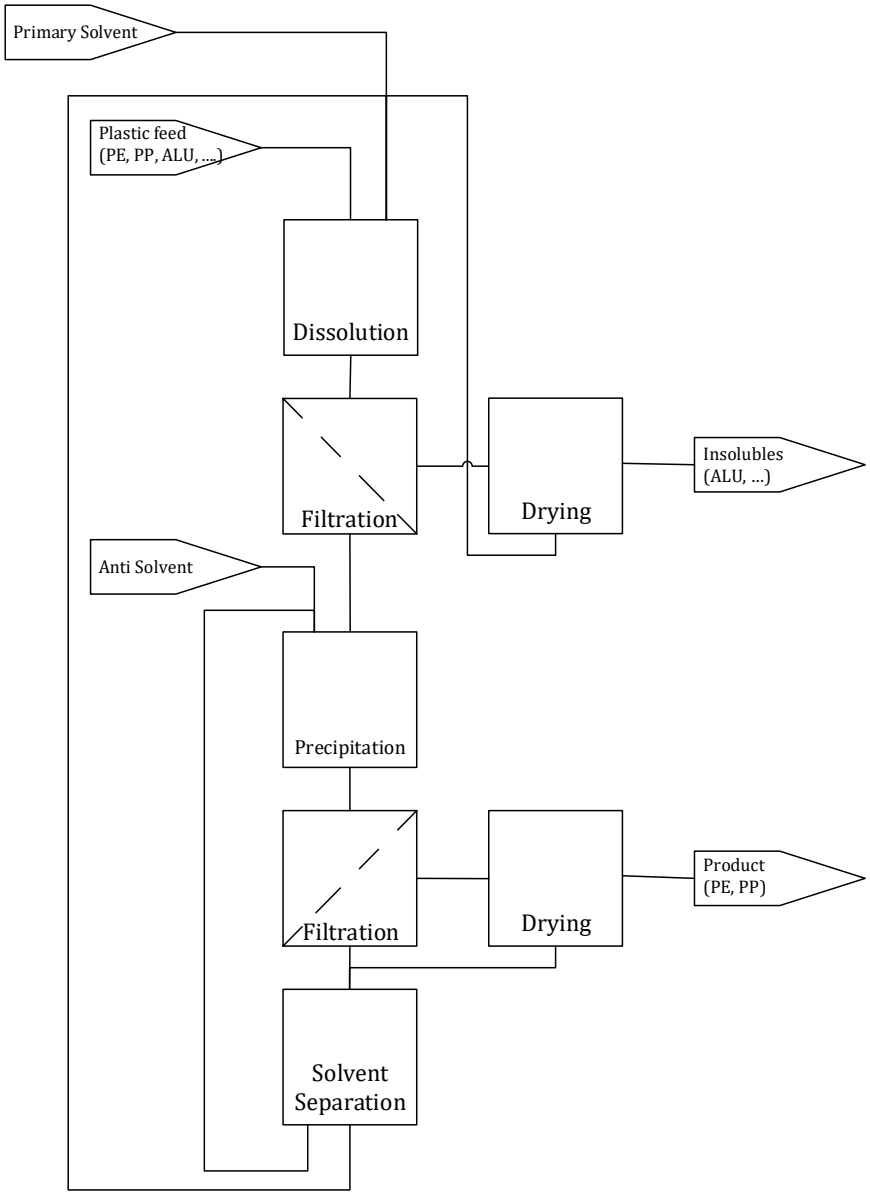

Figure 3 Process flow diagram of the TNO Möbius dissolution technology as designed for CIMPA.

The TNO TRL5 pilot (TNO Möbius Leto) was designed according to the PFD in Figure 3. Delays in the construction process of this pilot were encountered, specifically due to subcontractors extending delivery times of crucial units of operation by more than nine months (not delivered yet in the moment of writing this report). For this reason, a temporary purposely built CIMPA pilot was realized that fulfils the requirements of TRL5 operation and allows for all processing steps as depicted in the PFD. Nevertheless, there are some key differences in the operation of the temporary CIMPA pilot, such as generally more labour intensive

process due to limited automation of the process, lower surface area to volume ratio of the dissolution step, other type of stirring, smaller diameter of pipes. A lot of effort was invested in the commissioning of the CIMPA pilot as in this case, a scale-up based on significantly bigger units/vessels brings new challenges that need to be addressed in contrast to the TRL4 operation, *e.g.* change in the heat transfer, adaptation of the residence time for the dissolution and filtration step, variation in the configuration of particular processing steps to achieve target quality of the product. In addition, the large volumes of solvent required an extensive safety study (HAZOP) and set strict requirements on explosion safety within the scope of the ATEX regulation. These safety studies were part of the design phase and during commissioning, where operation according to specifications and required certification had to be verified. The CIMPA pilot was commissioned in May 2024 and in operation until September 2024.

The sorted, pre-treated metallized PO-rich film waste was delivered by AIMPLAS, two batches of 23 kg in total (Figure 4).

Figure 4 Real metallized film waste sample after pre-treatment by AIMPLAS.

VTT analysed both batches by DSC and XRF to determine their composition before any process. The thermograms in Figure 5 show that different PE grades, PP and PET can be seen, as well as some variation between the different batches. The polymer fraction of the material amounts to approximately 98%, remaining 2% coming from metals present in the film (predominantly aluminium from the metallised foils and titanium from TiO_2 filler) as indicated by XRF analysis in Figure 6. The relative compositional analysis of the 1st batch indicated 56% PE, 35% PP and 9% other polymers (mainly PET), the 2nd batch has not been quantitatively analysed but somewhat higher PP content is expected. As both PE and PP will be recovered in the dissolution process, a precise distribution of individual PO fractions is not relevant, the product will be a mix of PE and PP.

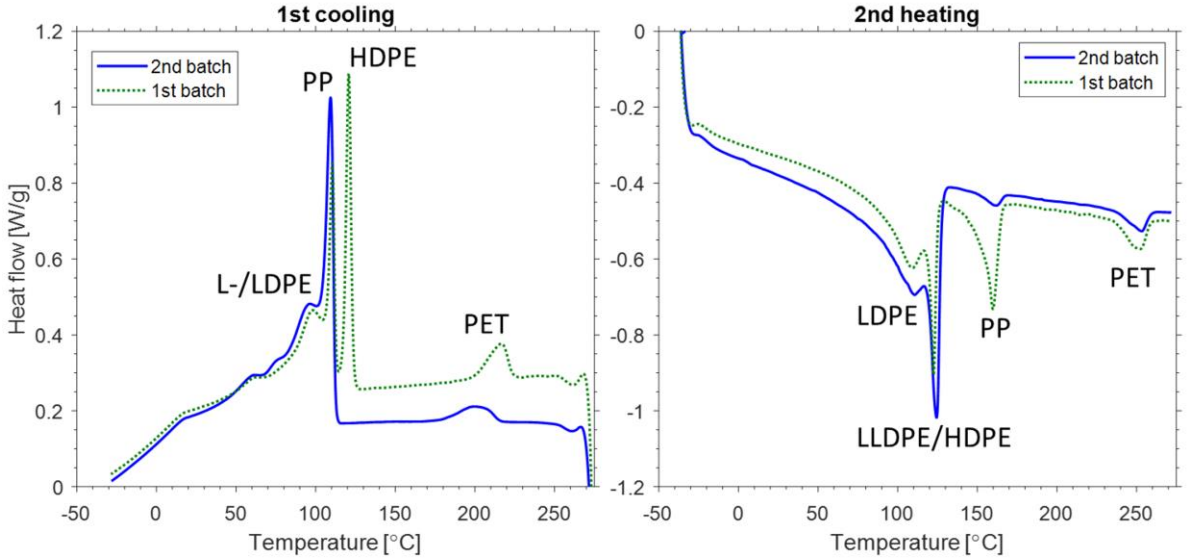

Figure 5 DSC analysis of the pre-treated metallized waste sample. Comparison of 1st and 2nd batch.

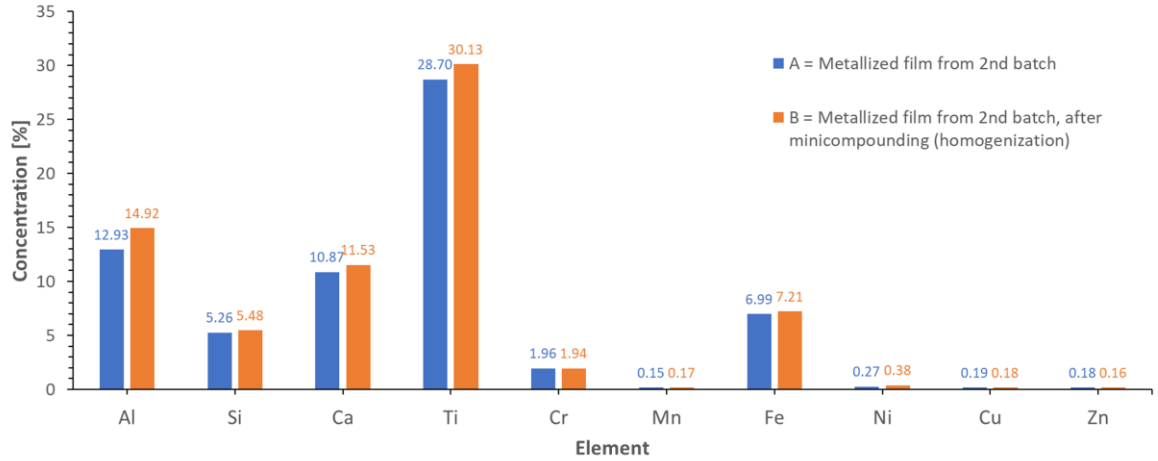

Figure 6 XRF analysis of the 1st and 2nd batch of metallized film.

The dissolution process applied to the metallized films proceeded according to the method established in the process development phase at lower TRL with further adaptation of the process parameters to reach the desired performance of the process at TRL5. The waste material was loaded into the dissolution vessel together with chosen low-boiling point organic solvent that selectively dissolves polyolefins. The dissolution took place at elevated temperatures, above the atmospheric boiling point of the solvent resulting in a pressurized system. Tests on the real waste at lab scale showed that about 10 wt% of the material remains undissolved in the process. These insolubles are predominantly other non-PO polymers such as PET, aluminium and pigments as supported by analytical results of the metallized waste sample. The insoluble part of the waste material is removed by a coarse filter. The polymer solution is then transferred towards the fine-filtration unit.

In the fine filtration step, the polymer solution is further purified to achieve the removal of fine impurities such as residual metals and colourants.

Finally, the purified polymer is recovered by adding anti-solvent (non-solvent for polyolefins) that leads to a decrease in solubility of the PO polymers in the solution and when a sufficient amount of anti-solvent is used, the polymer precipitates from the solution. The precipitated polymer was subsequently filtered from the solvent and dried in a vacuum oven. The solvent was collected for further recycling and reuse. Figure 7 shows an example of recovered PO product from one of the process batches in the form of bigger agglomerates. The agglomerates are further milled to achieve a powder-like consistency, homogenize the sample and allow for its further processing in the recompounding step.

Figure 7 Example of PO product as received in one of the process batches. Left: Recovered precipitated polymer in bigger agglomerates. Right: milled polymer product in a powder-like form.

Dissolution-based recovery process for polyolefins from complex multilayers at TRL 5

The experiments performed at TRL5 in the period of 05/2024 to 09/2024 were all done with the main goal of providing a physically recycled material that can be further recompounded at VTT and used in the production of demonstrator films at Barbier. The aim was to process about 15-20 kg of sorted, pre-treated metallized film waste to recover about 10-14 kg of recycled PO of high quality achieved by removal of all non-PO materials, additives and impurities. Due to the delays in the realization of the TNO Möbius Leto pilot, a purpose built TRL5 CIMPA pilot was used to fulfil the set goals of CIMPA for physical recycling.

Several challenges were encountered during the scale-up of the technology while using this CIMPA TRL5 pilot. Failures of critical instrumentation during the operation took place delaying the production (*e.g.*, temperature sensors, critical valves, pressure indicators) as well as numerous cases of clogging occurring in various parts of the set-up due to the gelation of polymer. The gelation of the PO is highly unexpected as it was not observed before under the conditions used and is therefore not understood. For this reason, several revamp sessions of the set-up

had to take place to minimize the impact of the gelation on the processing of the material. In each revamp of the set-up, a new configuration and/or set of processing parameters were put in place and tested. It was an iterative and very time-consuming process. As a result, only approximately 6 kg of waste material was processed in total of 9 batches. The process yield significantly varied per batch, from no recovered material in case of total system upset to typically up to 17 wt% in case of clogging taking place in some of the processing steps. Finally, the right combination of process configuration and parameters for the temporary CIMPA TRL5 pilot was found and a product yield of 70 wt% was reached in the last processed batch. Unfortunately, due to time and budget constraints, no additional batches of the material could be processed within this project. The physical recycling process executed in this pilot has produced 1.02 kg of recycled PO as shown in Figure 8. However, a lot of experience could be gained from these experiments about handling the waste material at this TRL and further upscaling of the process, which will be implemented in follow-up projects..

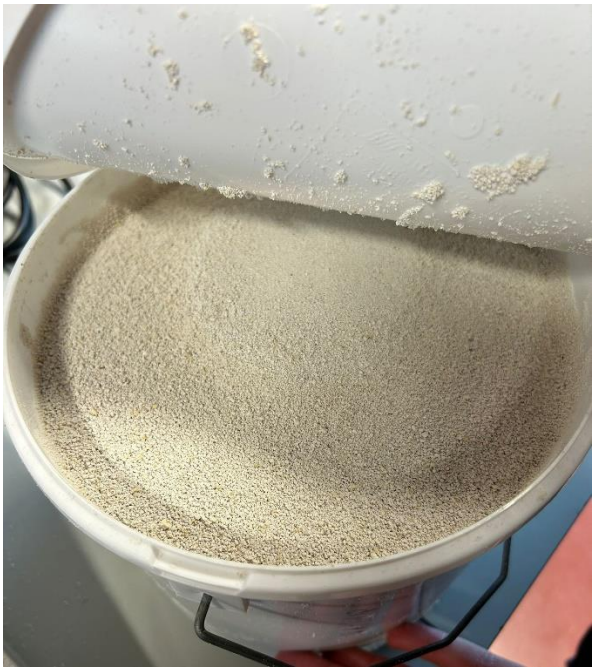

Figure 8 Polyolefin product recovered from the CIMPA TRL5 pilot.

Dissolution product analysis

The recovered PO product was analysed for solvent content to establish if further decontamination by AIMPLAS if necessary. It was concluded that only devolatilization is necessary, and decontamination is not needed, as the dissolution process already decontaminates the PO. The TGA analysis showed no residual solvent in the product, allowing for direct recompounding by VTT without any devolatilization (Figure 9).

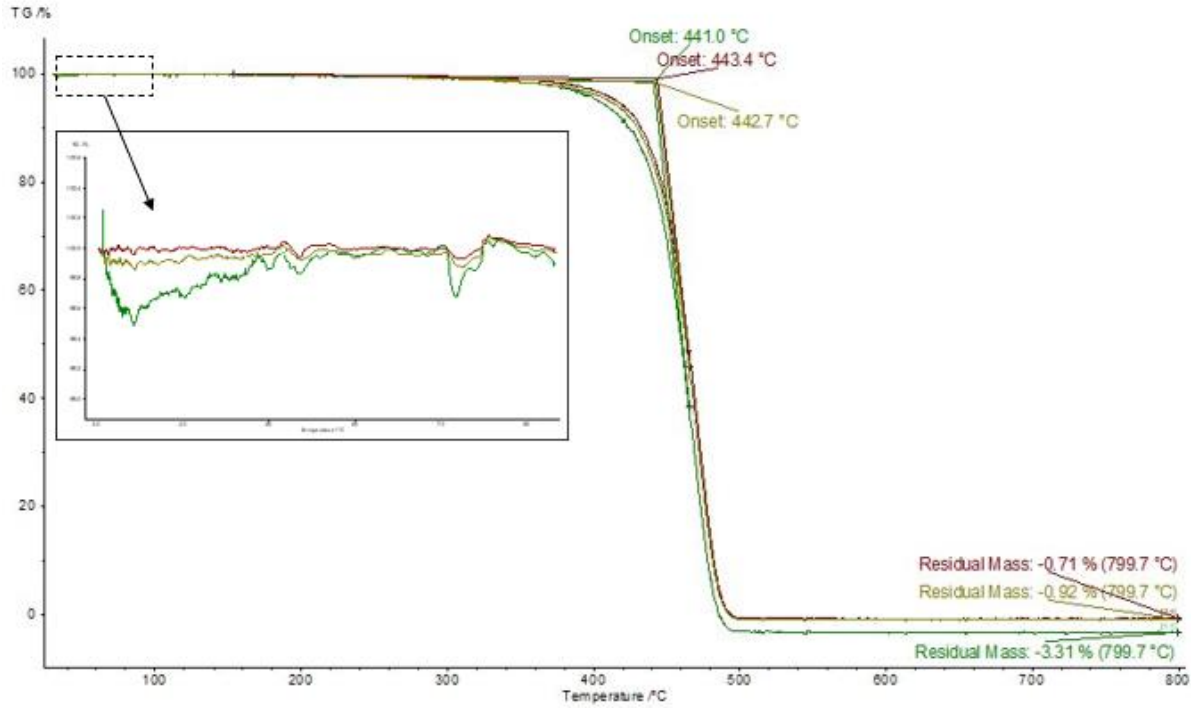

Figure 9 TGA curve of the PO product from CIMPA TRL5 pilot. 3 parallel samples measured. Zoom-in on temperature range where residual solvent evaporation could be measured.

Further analysis, namely FTIR, XRF and DSC, were performed on the product from physical recycling. FTIR analysis provided information about the sample composition (i.e. which polymers are present in the product), whereas XRF focused on the elemental analysis shedding light on the presence of inorganic contaminants. The FTIR spectrum of the product (as shown in Figure 10) is consistent with PE (LDPE and HDPE detected) and isotactic PP. No other polymers were detected.

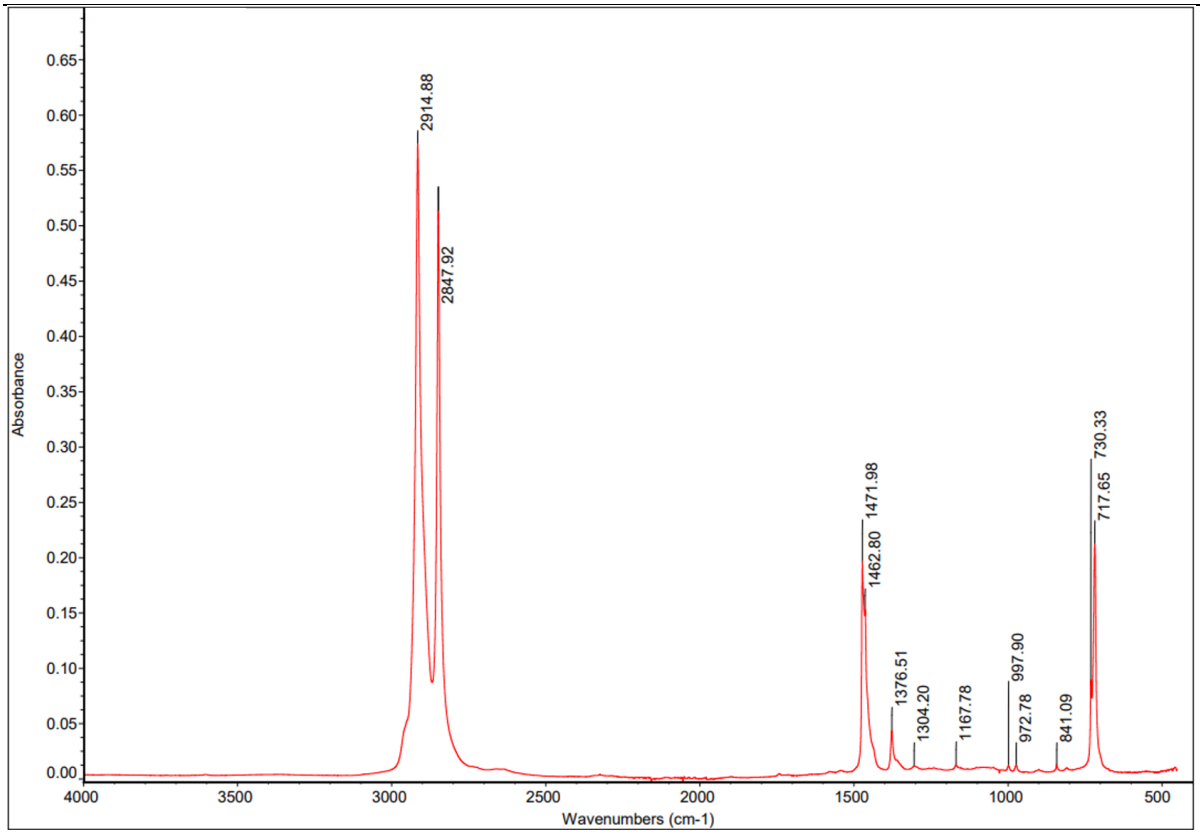

Figure 10 FTIR analysis of recovered PO product in CIMPA TRL5 pilot.

The recovered product was pressed into pellets and further analysed by XRF. The analysis shows high purity of the recovered product with only trace amount of inorganic material (Fe) obtained in first 7 batches as can be seen in Table 1. Low amounts of detected Fe very likely originate from the set-up due to adaptations in the configuration and/or replacement of parts. It is not expected that any residual Fe would be detected when the process runs continuously. However, the process yield from the first batches was very low, often caused by system clogging or overall malfunction as discussed previously. For this reason, the process parameters were continuously adapted and the quality of product varied accordingly. Finally, in order to reach higher quantities of the product and prevent the system clogging, the fine filtration step was significantly simplified. As result, last two batches have poorer quality than previous ones but reaching process yield of 70%. At this point, there is a clear trade-off between recovered product quantity and quality. In all processed batches, aluminium was successfully removed. Finally, all process batches were combined to reach higher quantity of product. The mixed batch of PO product was analysed as well (Figure 11). The quality is determined/affected by the batch #9 which was the biggest in the volume and contributed then the most towards the impurities in the product.

Table 1 XRF analysis of PO product from CIMPA TRL5 pilot per batch.

Element (ppm)/batch	2	3	4	5	6	7	8	9	mix
Fe	67 ± 7	42 ± 3	30 ± 1	215 ± 22	45 ± 3	84 ± 13	211 ± 6	183 ± 16	169 ± 9
Ti		7 ± 6		74 ± 37	140 ± 13	9 ± 5	1166 ± 54	1315 ± 16	1014 ± 26
Cr		10 ± 8		35 ± 8		9 ± 7	18 ± 2	13 ± 6	18 ± 2
Ni				12 ± 2			7 ± 1	11 ± 2	7 ± 1
Cu				3 ± 1			10 ± 0	12 ± 1	8 ± 0
Ca					93 ± 20		609 ± 33	487 ± 11	378 ± 11
Zn							19 ± 0	18 ± 1	13 ± 0

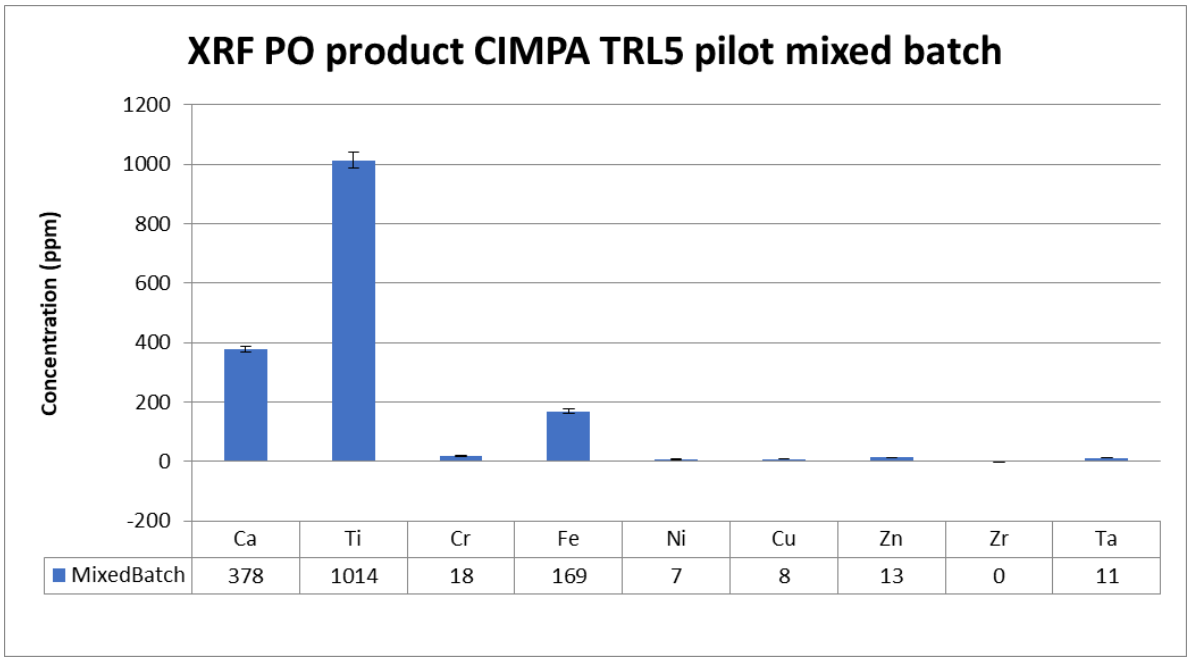

Figure 11 XRF analysis of PO product from CIMPA TRL5 pilot, mixed batch.

DSC analysis of the product provides information about the thermal stability of the sample as well as its composition. DSC-OIT analysis performed in the course of the project confirmed (partial) removal of antioxidants in the dissolution products. For this reason, stabilisers need to be re-introduced before a recompounding step to restore the thermal stability. This was done during re-compounding by VTT.

Based on established calibration curves, the presence of LDPE, LLDPE and PP was quantified in the recycled product (Figure 12). Approximately 20.6 % of PP was measured in the product with a PE/PP ratio of approx. 3.9. The PE/PP ratio of lab scale batches lied in the range 1.9 – 2.3. The amount of PP relative to PP decreased

in the recycled product received from CIMPA TRL5 plant. A significant gel formation and clogging was observed during the plant operation. As the solubility of PP is lower than PE at operating conditions applied, it is expected that some of the PP got retained in the formed gel and/or clogged pipelines and filter. Hence, this PP was not recovered and consequently relatively less PP was found in the final product.

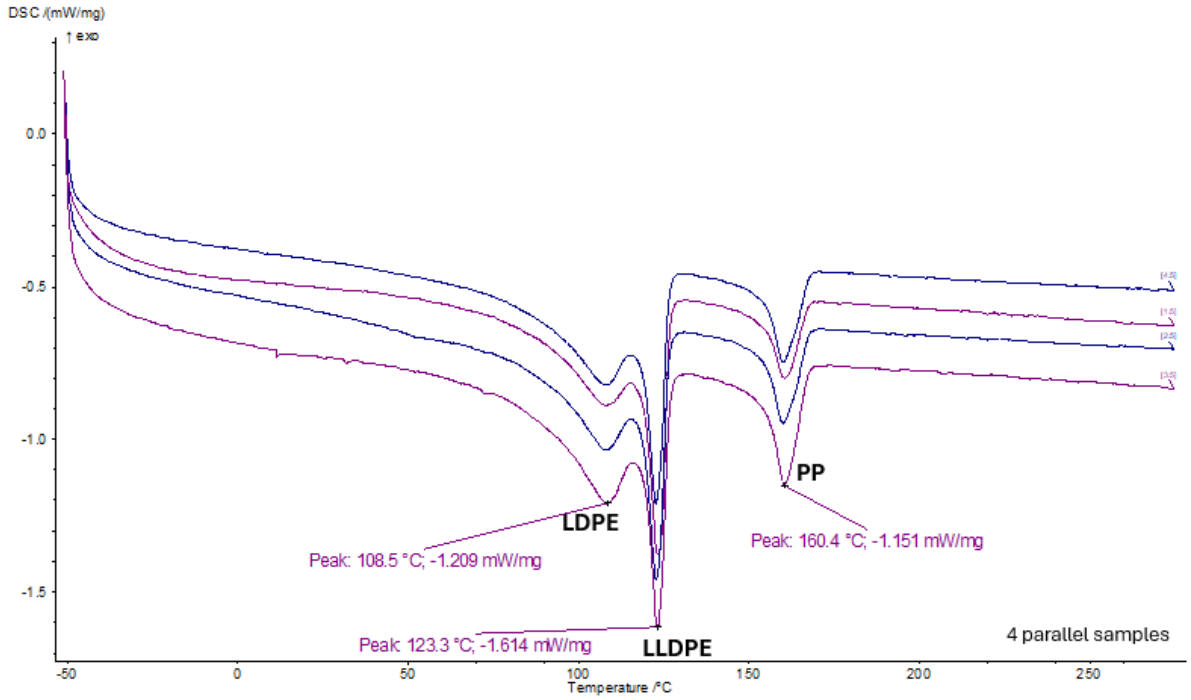

Figure 12 DSC analysis (2nd heating) of the PO product from CIMPA TRL5 pilot. 4 parallel samples measured.

By combining these analytical techniques, all key information about the product necessary for the evaluation of the physical recycling process were obtained.

Conclusion and next steps

In this deliverable, a physical recycling process for recovery of polyolefins from complex multilayer materials, i.e. metallized films, at TRL5 was presented.

- The physical recycling process developed in the CIMPA project was successfully realized at TRL5 by building a pilot that can process kg scale of complex multilayer waste safely.

- The experiments done at the TRL5 pilot were used to provide recycled PO material for recompounding and further testing in WP5.

- During the experimental campaign, the feasibility of the physical recycling process concept for processing waste material at kg scale could be proven as a total of 6 kg sorted post-consumer waste was processed to provide 1 kg of dry recycled PO. Several major setbacks were encountered during the scale-up of this novel technology and the experimental campaign, resulting to lower amount of recovered polymer. However, the project concept has been proven at a kg scale.

- It has been proven at both lab scale and TRL5 that physical recycling leads to a high purity of product with no residual solvent avoiding the need for an additional devolatilization and decontamination step. This aspect leads to benefits in both economic and environmental performance of this recycling technology.

- Until project end in November 2024, demonstrator films will be produced from this recycled PO material with the help of partners VTT, Leygatech and Barbier.