Upgrading polyolefin and engineering plastics recyclates for use in flame retarded high-value applications

Dr. Michael Großhauser
Fraunhofer-Institute for structural durability and system reliability LBF

Agenda

- Fraunhofer LBF
- Motivation
- Evaluation of recyclate quality
- Project implementation and results
- Summary and take home massage

  Open

Fraunhofer LBF

01

Fraunhofer LBF

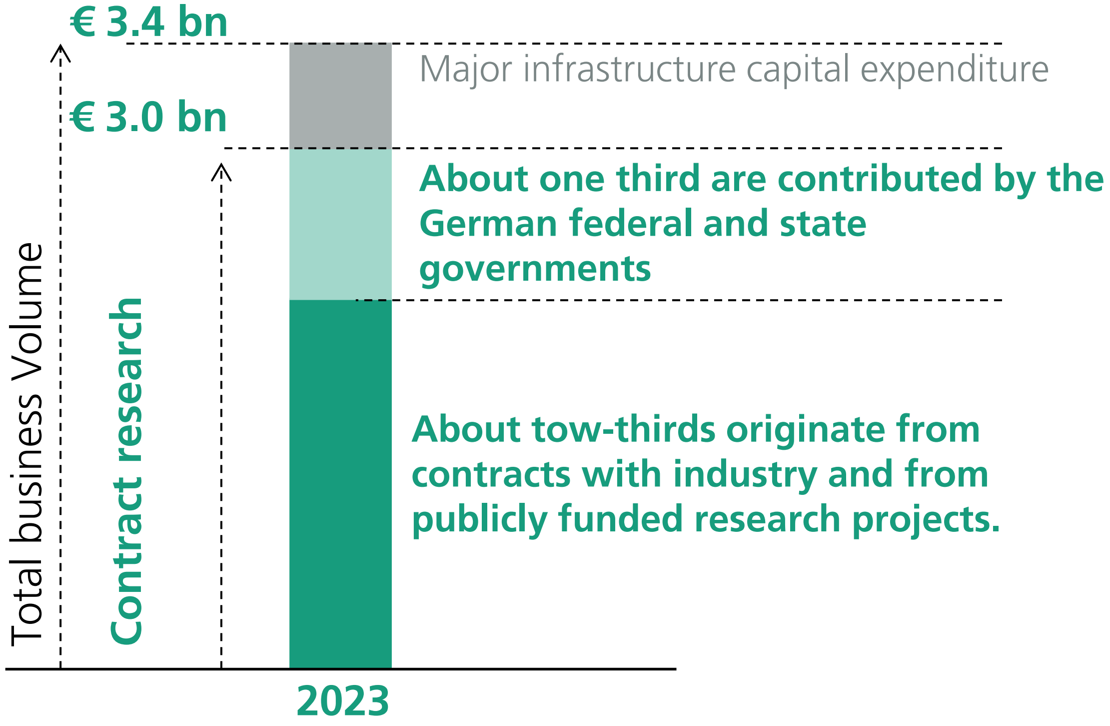
The Fraunhofer Gesellschaft

Facts and Figures 2023

The Fraunhofer-Gesellschaft conducts applied research of direct benefit to private and public enterprises and of great benefit to society.

About 32000
Employes

76 Institutes and
Research Institutions



  Open

Fraunhofer LBF

Research Division **Plastics**

Dr. rer. nat. Elke Metzsch-Zilligen

Objectives

Within the research division all the competencies relevant to the realization of high-end plastics applications are united. Starting with the fundamental scientific disciplines such as chemistry and physics, through materials science and materials engineering in processing, to expertise in analytics, testing and modeling.

Research activities

- Synthesis and formulation
- Additivation and durability
- Material analysis and characterization
- Plastics processing and component design

> **»With specific additive solutions as the key to polymer technology innovations, we design sustainable high-performance materials for technical product solutions!«**
>
> **Dr. rer. nat. Elke Metzsch-Zilligen**
> Head of Division

02

Motivation

European framework

- **Circular economy action plan 2015: „Closing the loop“**
- Increasing recycling efficiency
- Expand best practices in waste management and resource efficiency
- Development of a new framework for waste management
- Quality standards for secondary raw materials
- Improving waste management in line with the waste hierarchy

- **EU plastics strategy**
- Adopting an EU strategy for plastics in a circular economy to reduce plastic waste.
- Set ambitious targets for the recycling of plastics.
- Communication on the interface between chemicals, product and waste legislation.
- Establish a monitoring framework for the circular economy.
- Reporting on critical raw materials and on oxo-plastics.

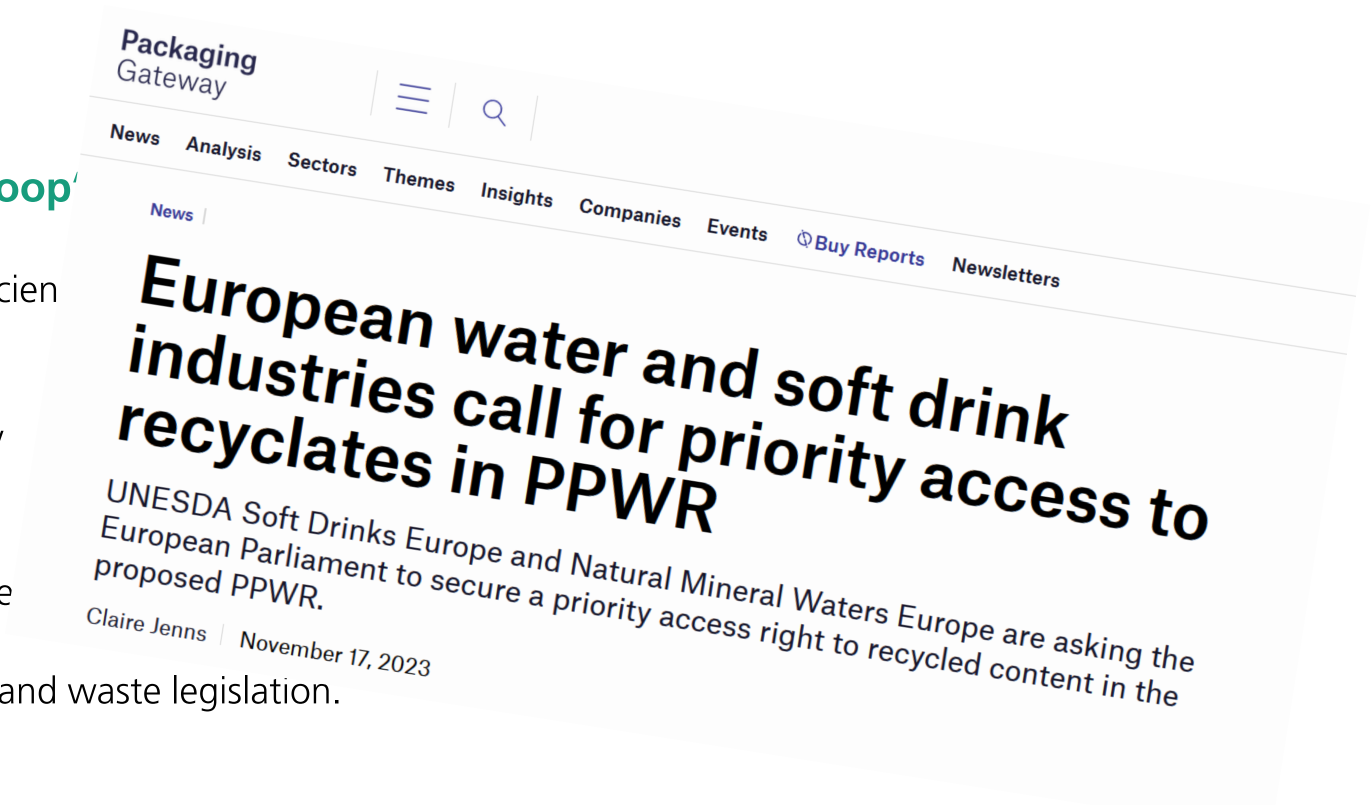
- **EU End of Life Vehicle Regulation (ELVR)**
- 13th July 2023 proposal for a new regulation
- **25% Post Consumer Recylates PCR (incl. 25% Closed Loop)**

European framework

- **Circular economy action plan 2015: „Closing the loop“**
- Increasing recycling efficiency
- Expand best practices in waste management and resource efficien
- Development of a new framework for waste management
- Quality standards for secondary raw materials
- Improving waste management in line with the waste hierarchy

- **EU plastics strategy**
- Adopting an EU strategy for plastics in a circular economy to re
- Set ambitious targets for the recycling of plastics.
- Communication on the interface between chemicals, product and waste legislation.
- Establish a monitoring framework for the circular economy.
- Reporting on critical raw materials and on oxo-plastics.

- **EU End of Life Vehicle Regulation (ELVR)**
- 13th July 2023 proposal for a new regulation
- **25% Post Consumer Recylates PCR <u>(incl. 25% Closed Loop)</u>**


Packaging Gateway

News Analysis Sectors Themes Insights Companies Events Buy Reports Newsletters

News

European water and soft drink industries call for priority access to recyclates in PPWR

UNESDA Soft Drinks Europe and Natural Mineral Waters Europe are asking the European Parliament to secure a priority access right to recycled content in the proposed PPWR.

Claire Jenns | November 17, 2023

[3] „European water and soft drink industries call for priority access to recyclates in PPWR“, Packaging Gateway, https://www.packaging-gateway.com/news/european-water-soft-drink-industries-priority-access-recyclates-ppwr/, 18.07.2024

  Open

Fraunhofer LBF

Whats the amount of recyclates in the market?

- **The amount of plastic components is increased in electric cars, therefore it will rise from average 200 kg in 2020 to 400 kg in 2025.**

- **Status in Germany:**

German plastic market 2021	Total quantity (kt)	Virgin material (kt)	Recycled material (kt)	Quota today	Future quota	Needed recyclates (kt)
Packaging	4.378	3.708	670	15.3 %	40.0 %	1.751 (+1.081)
Vehicles	1.230	1.160	70	5.7 %	25.0 %	308 (+238)
Electro/Electronics	895	855	40	4.5 %	20.0 %	179 (+139)

- **Status in Europe:**

9.5 mt of plastics were colletected for recycling by E28+2, while 2.0 mt come from non-packaging. Still 5.4 mt of non-packaging plastics go to incineration!

[1] Stoffstrombild Kunststoffe in Deutschland 2021, Conversio, Oktober 2022

But how can we reach the quotas? Recycling of flame retarded plastics!

- **hffr plastics are recyclable!**
- **Project/study at Fraunhofer LBF with support by Pinfa, from 2015 -2018, showed the stability of the flame retardants in compounds during simulated recycling processes.**
- **Even FR compounds with degraded polymeric matrices after accelerated aging and/or multiple extrusion showed V-0 classifications in the UL-94V tests.**
- **What happens when there are mixtures and impurities in the compounds?**

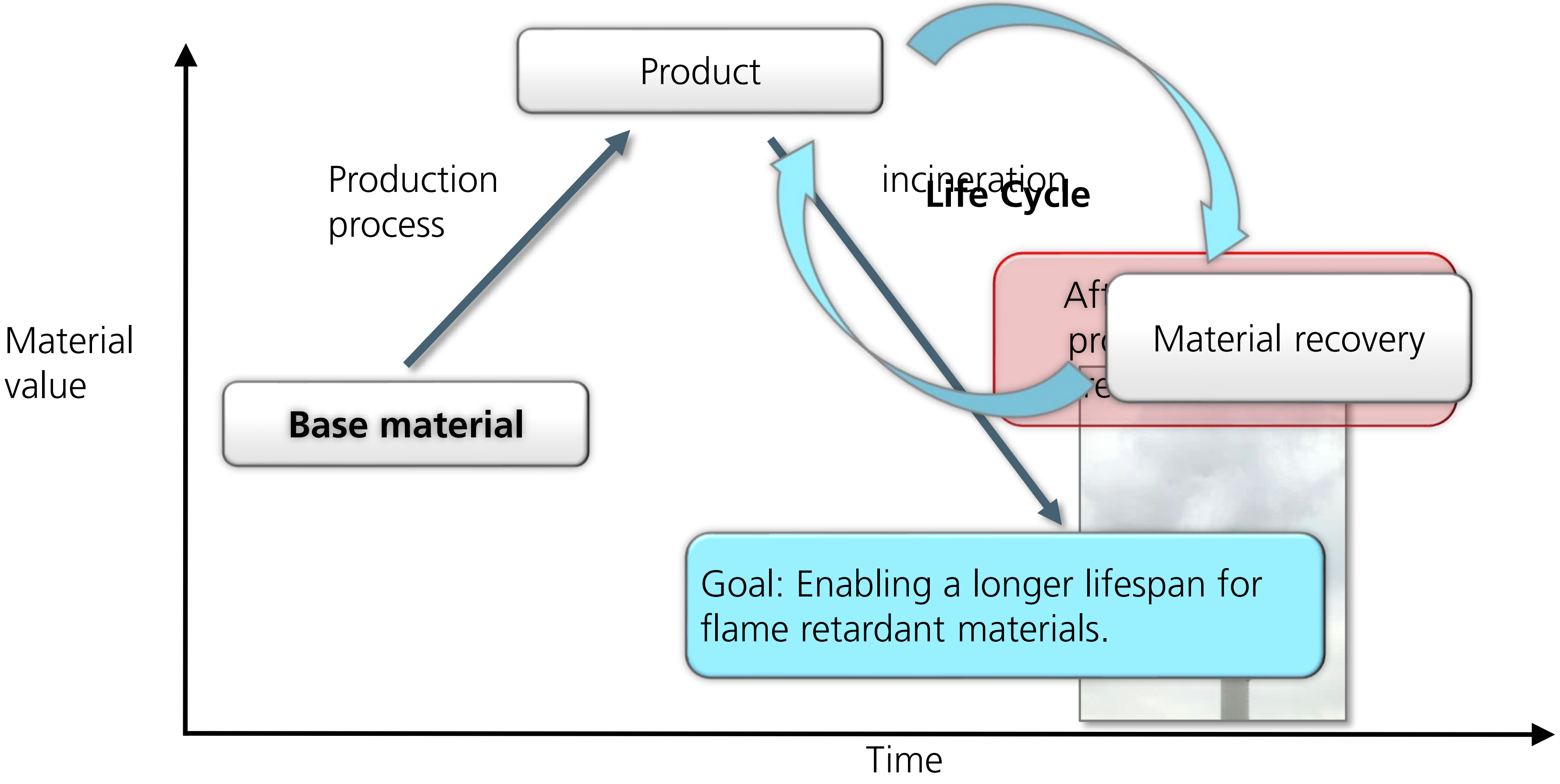
Fraunhofer LBFs and PINFAs research activities on the recycling of plastics containing halogen free flame retardants

Recycling is an important issue with regard to the sustainable use of our limited resources. Only a few materials can theoretically be as easily recycled as plastics. Due to the use of different additives and specialized production processes, depending on the needs of the end application, recycling of plastics has become more and more complex. Flame retardants are a good example for additives which have to be used for different long-time applications. Due to different known advantages, halogen-free products are the flame retardants of choice.

With regard to the recyclability of flame retardant plastics after their „end-of-life", it is of high importance to understand the influence of flame retardants on recycling. With this knowledge the development of new compatible flame retardants can be endeavored. For a better understanding, Fraunhofer LBF in Darmstadt, Germany, started a perennial project on this topic in October 2015. For the first time the recyclability of halogen free flame retardants plastics is investigated to find ways to recycle these materials and optimize the resulting polymers. At the same time this project adds a value

[2] „Fraunhofer LBFs and PINFAs research activities on the recycling of plastics containing halogen free flame retardants", FLAMERETARDANTS-ONLINE, https://www.flameretardants-online.com/news/?showid=18408, 18.07.2024

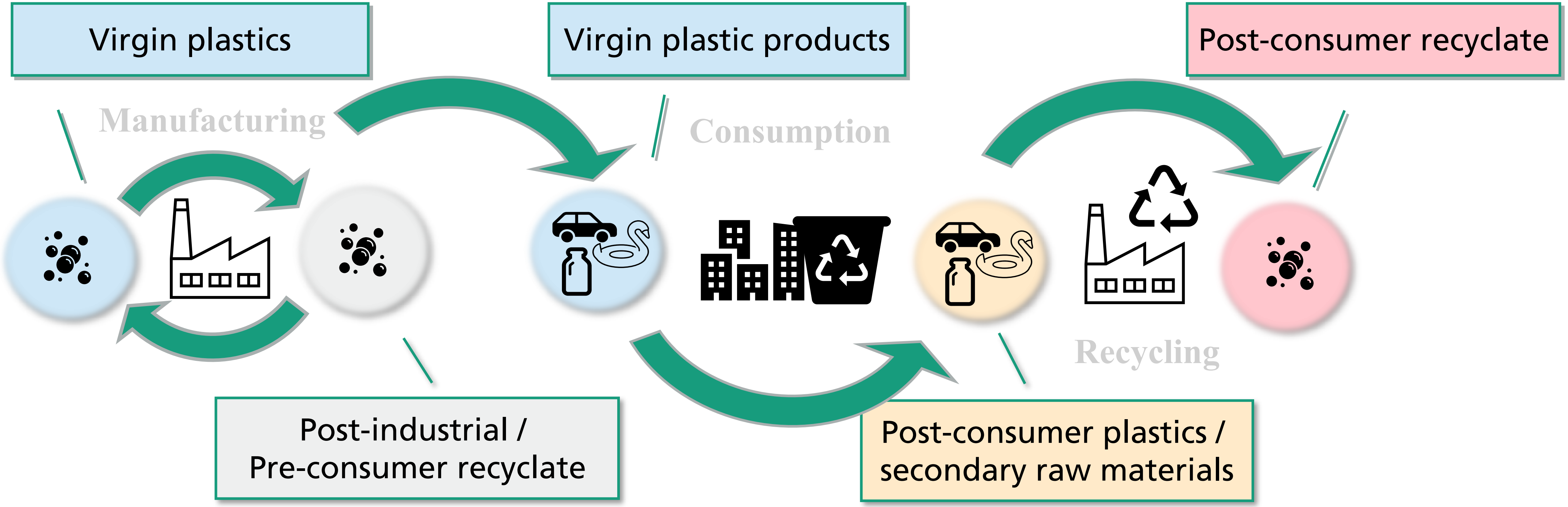
Where can I find the flame retarded plastics?



03

Evaluation of recyclate quality

Plastics in a recycling context

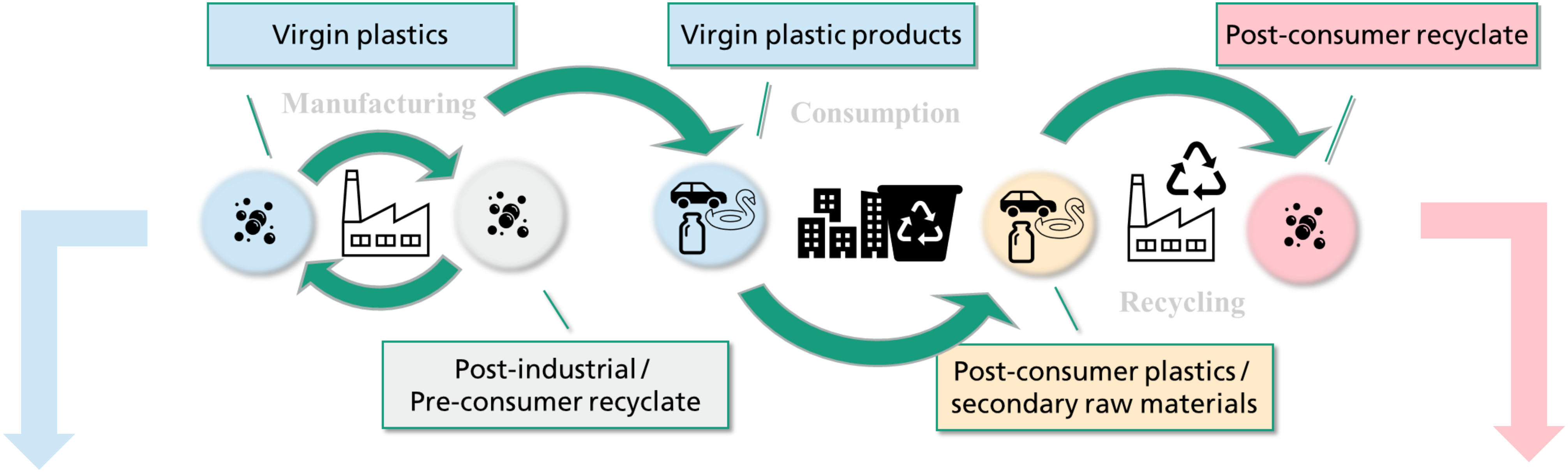


  Open

Fraunhofer LBF

Difference between virgin and recyclate

Analysis: virgin vs. recyclate

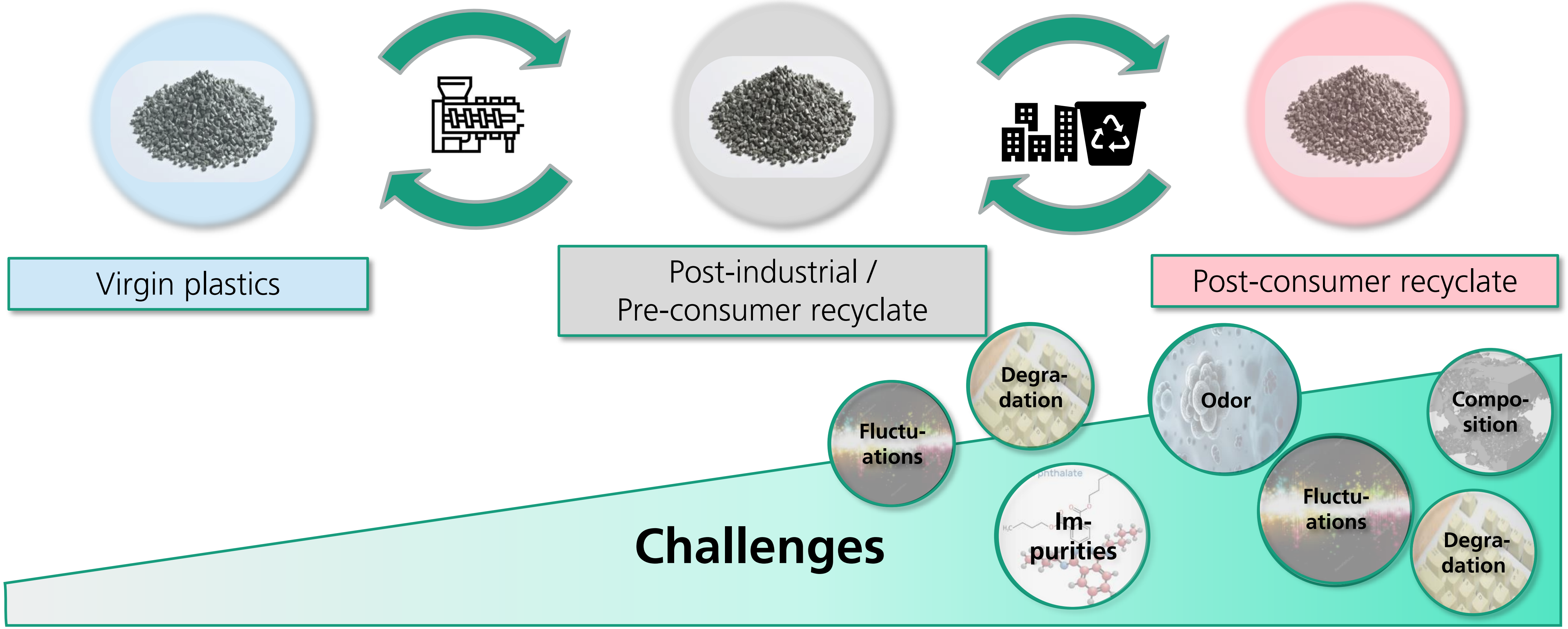


- Homogenity
- We know exactly what it is from the manufacturing process
- No external influences
- Characterization can be carried out without interfering factors

- Heterogenity
- Cannot estimate what is inside
- Many external influences
- Characterization must be carried out despite interfering factors

Challenges increase with material complexity

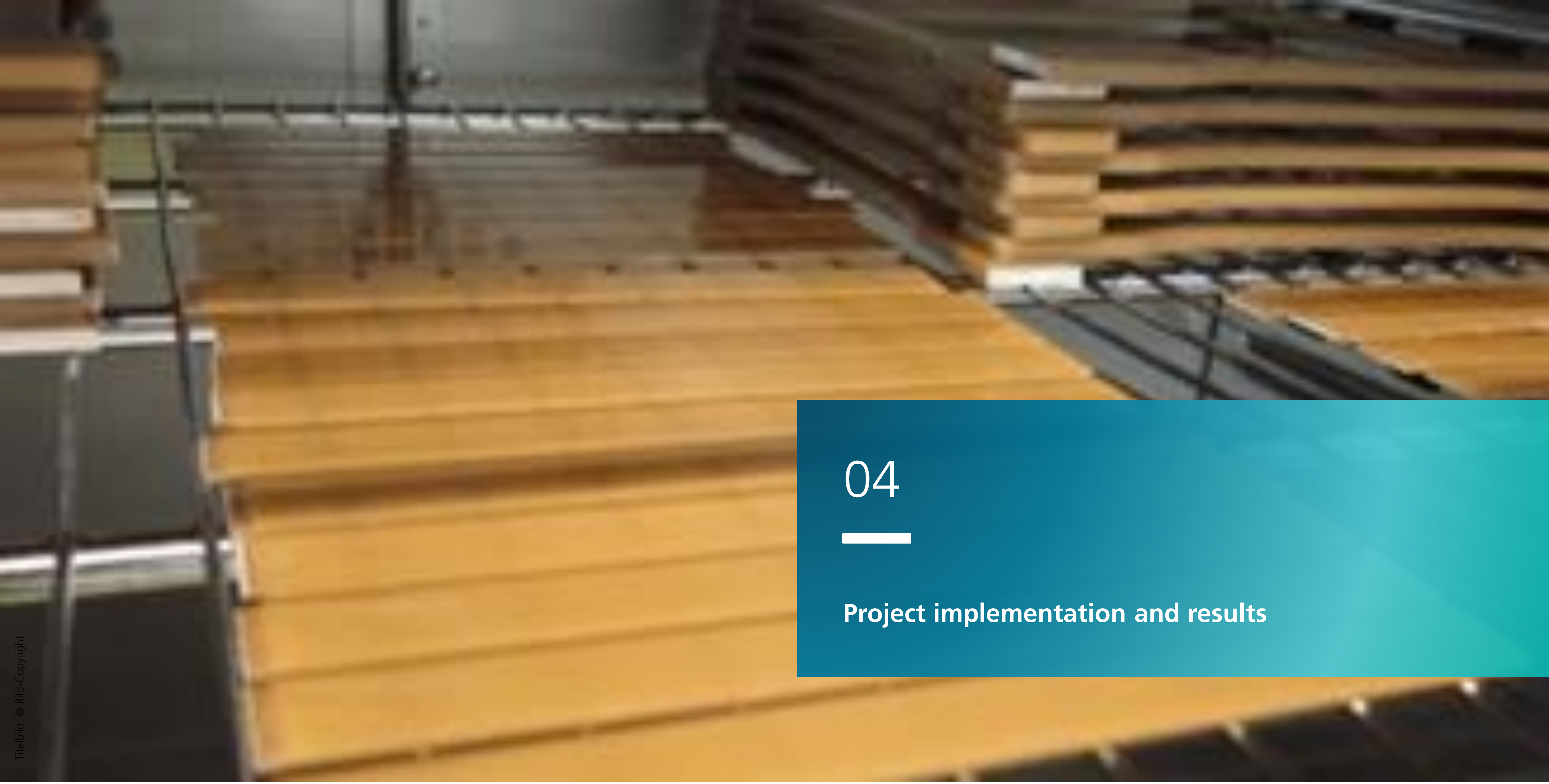
The use-phase complicates plastic's recycling



Quality evaluation of secondary plastics

Material analytics holds the answers

Material composition	NMR, (HT)-liquid chromatography, FTIR/Raman-spectroscopy, DSC, TGA, Pyrolysis-GC/MS	○ Identification of polymer impurities ○ Quantification of their amount ○ Evaluation of fluctuations
Impurities	NMR, FTIR/Raman-spectroscopy, liquid chromatography-MS, Pyrolysis-GC/MS, TGA	○ Identification of low-molecular weight components (VOC, SVOC, additives, …) ○ Identification of inorganic impurities
Degree of degradation	NMR, Melt flow analysis, mechanical testing, oxidation induction time, FTIR/Raman, liquid chromatography	○ Residual stabilization ○ Degree of chain degradation / branching/ cross-linking ○ Degree of oxidation

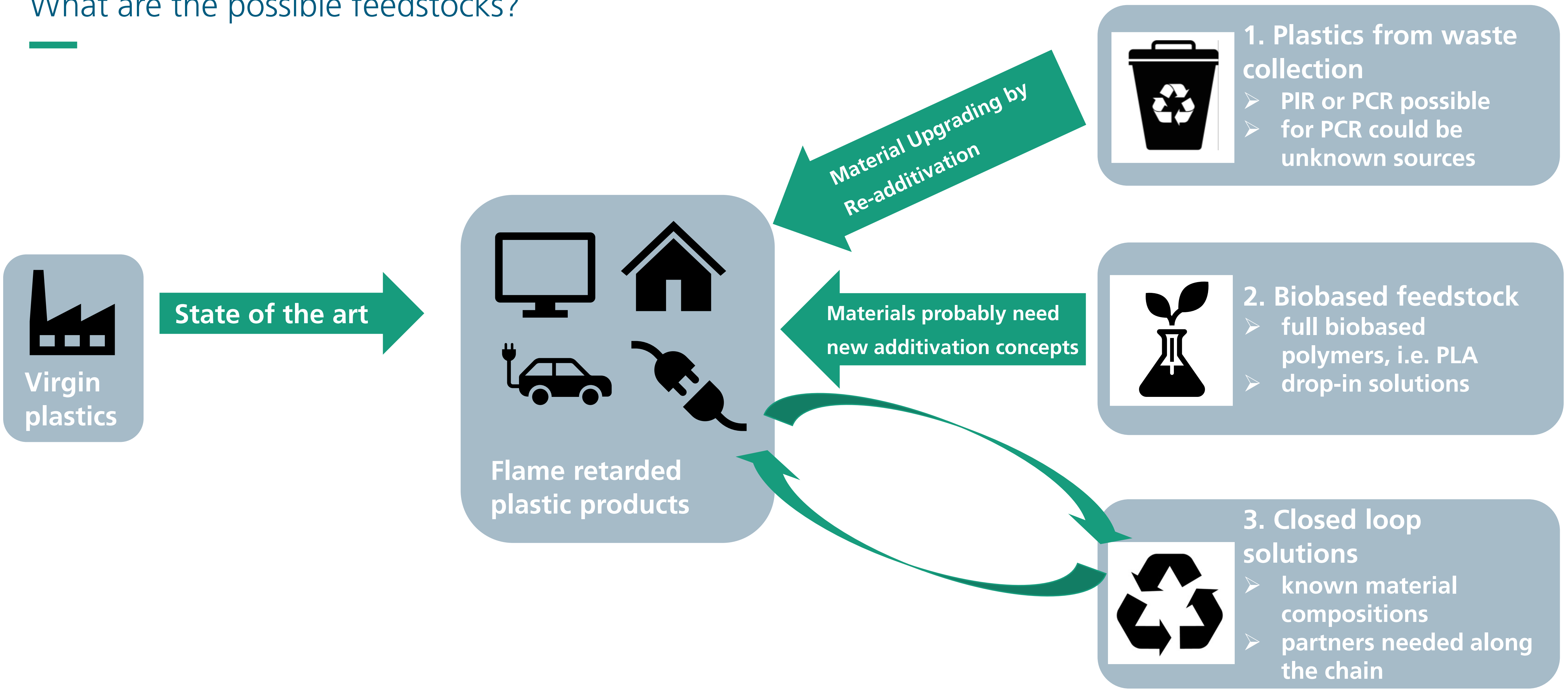


04

Project implementation and results

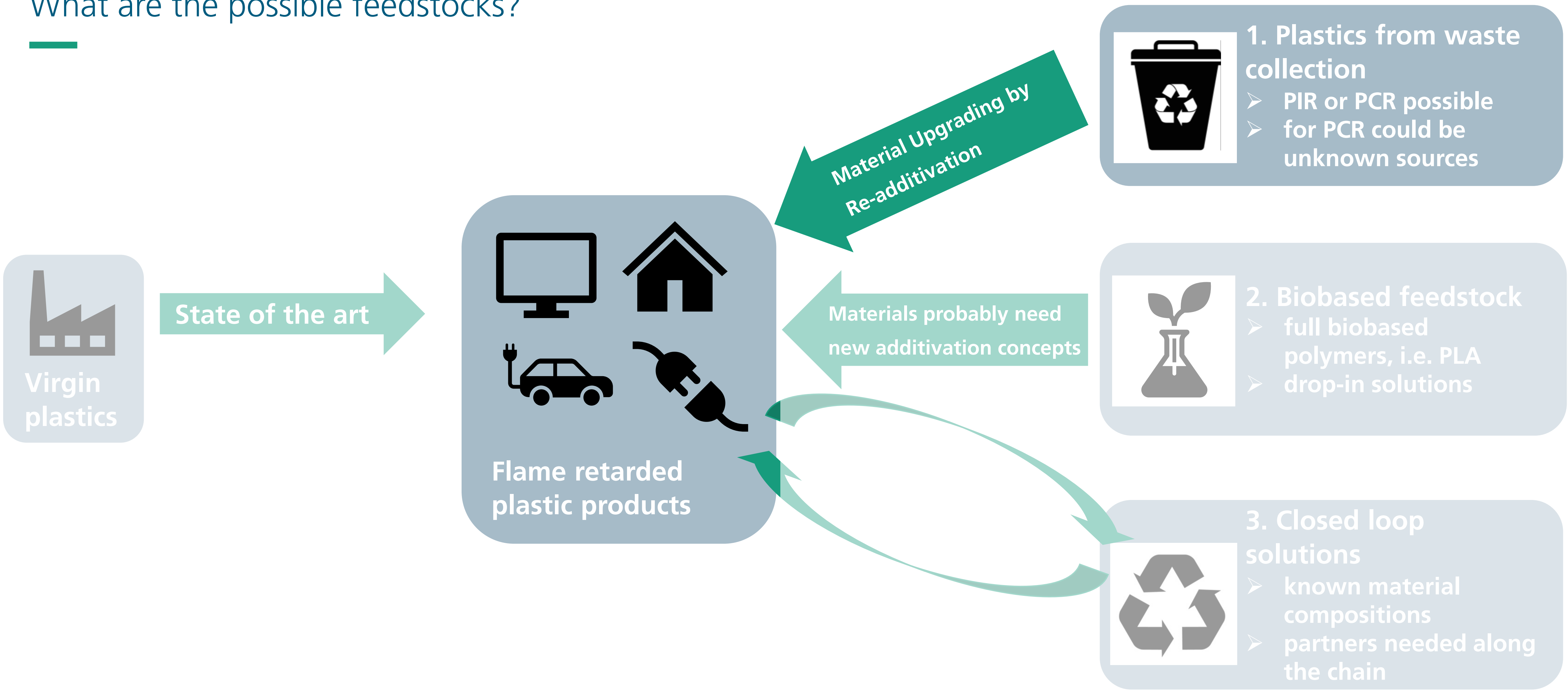
How to make flame retarded products more sustainable?

What are the possible feedstocks?



How to make flame retarded products more sustainable?

What are the possible feedstocks?

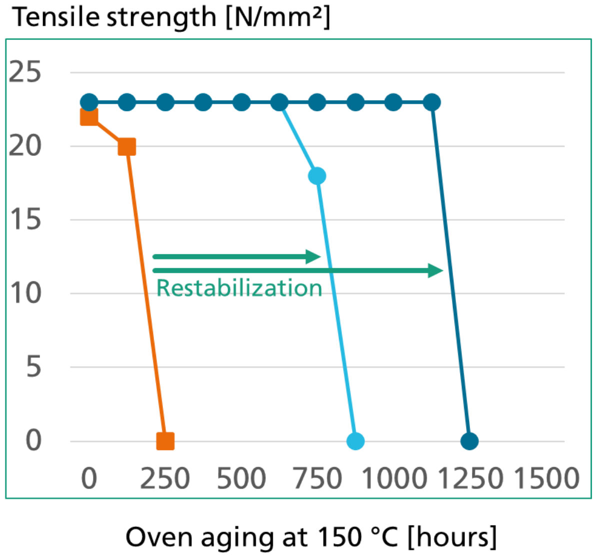


  Open

Giving plastics a new life: Re-additivation concepts

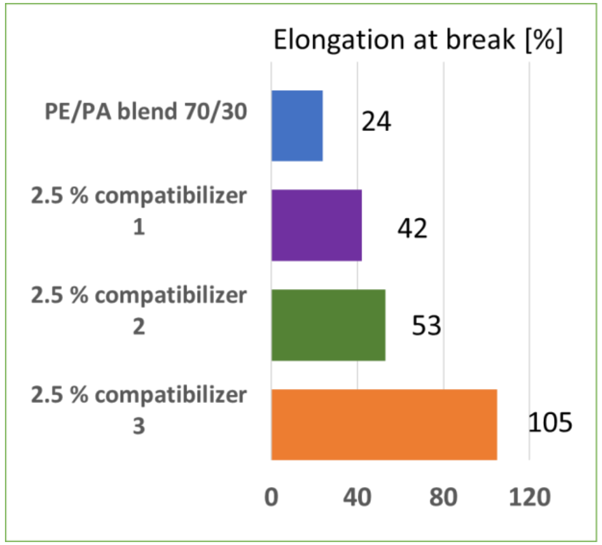
Formulation development on re-stabilization, compatibilization and chain extension

Re-stabilization



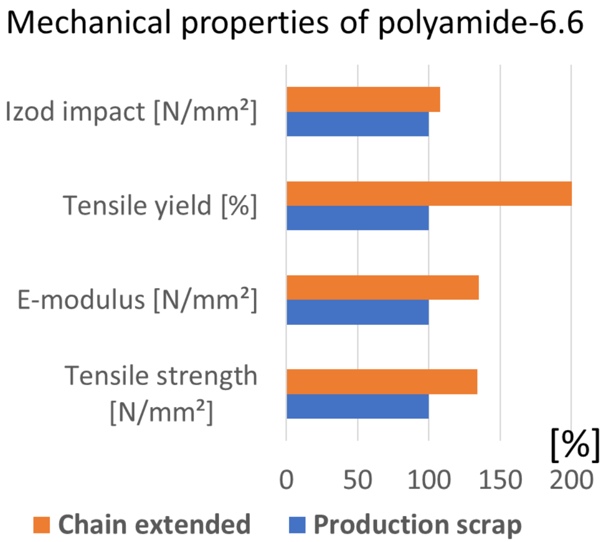
- All thermoplastic polymers
- Lifetime & recycling stability

Compatibilization



- Blends or PCR
- Composition-dependent

Chain Extension



- Polycondensates[4]
- Reactive extrusion, Repair

4 Herbst, H., Hoffmann, K., Pfaendner, R., & Zweifel, H. (1998). Upgrading of Recyclates—The Solution for High Value Applications: Restabilization and Repair. In Frontiers in the Science and technology of polymer recycling (pp. 73-101). Dordrecht: Springer Netherlands.

Objective of the project

Project was planned together with 10 companies as an industrial joint project. Companies that provide recyclates, Compounders, flame retardant producers, even direct competitors in the market, work hand in hand within this project.

Objectives:

- **Test the usability of market-available PIR or PCR for material upgrading into flame retarded plastic compounds.**
- **Are typical flame retardant formulations for specific applications work directly in recylates or is an adjustment needed?**
- **Evaluate which material flows are suitable for upcycling and how big is influence of the recyclate quality on the performance of the flame retardant.**
- **Investigate the long-term properties of the upgraded recyclates.**
- **Is it possible to fit the performance to current product standards?**

Project supported by following partner consortium

Material selection

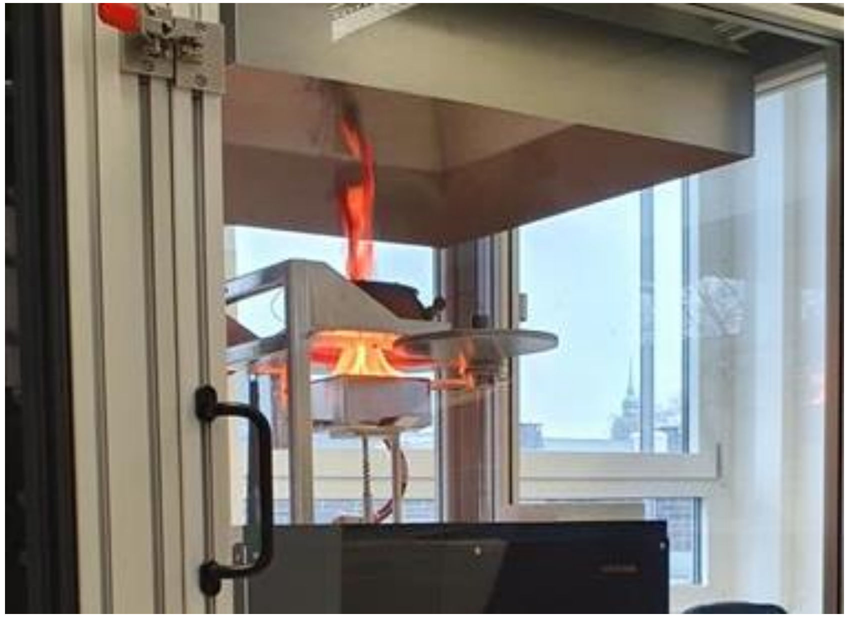
Polymer-Type	Application	Material source
Polypropylene (PP)	➢ Trunking/Conduits ➢ Housings ➢ Construction film	➢ PIR Packaging waste ➢ Furniture foil ➢ WEEE-Plastics from household collection at recycling centers
Polyethylene (LLDPE)	➢ Cable ➢ Construction film	➢ PIR Packaging waste
Polyamide (PA6 and PA66)	➢ Injection moulding application (motor management)	➢ PCR-PA6 from Fishnets ➢ PIR-PA66
Polyethylene-therephthalate (PET)	➢ Coil bobbin/sensor cover ➢ Injection moulding	➢ PIR-PET packaging films
Polycarbonat/Acrylnitril-Butadiene-Styrene (PC/ABS)	➢ Housings ➢ Injection moulding	➢ WEEE-Plastics from household collection at recycling centers

Material selection

Polymer-Type	Application	Material source
Polypropylene (PP)	➢ Trunking/Conduits ➢ Housings ➢ Construction film	➢ PIR Packaging waste ➢ Furniture foil ➢ WEEE-Plastics from household collection at recycling centers
Polyethylene (LLDPE)	➢ Cable ➢ Construction film	➢ PIR Packaging waste
Polyamide (PA6 and PA66)	➢ Injection moulding application (motor management)	➢ PCR-PA6 from Fishnets ➢ PIR-PA66
Polythylenetherephthalate (PET)	➢ Coil bobbin/sensor cover ➢ Injection moulding	➢ PIR-PET packaging films
Polycarbonat/Acrylnitril-Butadiene-Styrene (PC/ABS)	➢ Housings ➢ Injection moulding	➢ WEEE-Plastics from household collection at recycling centers

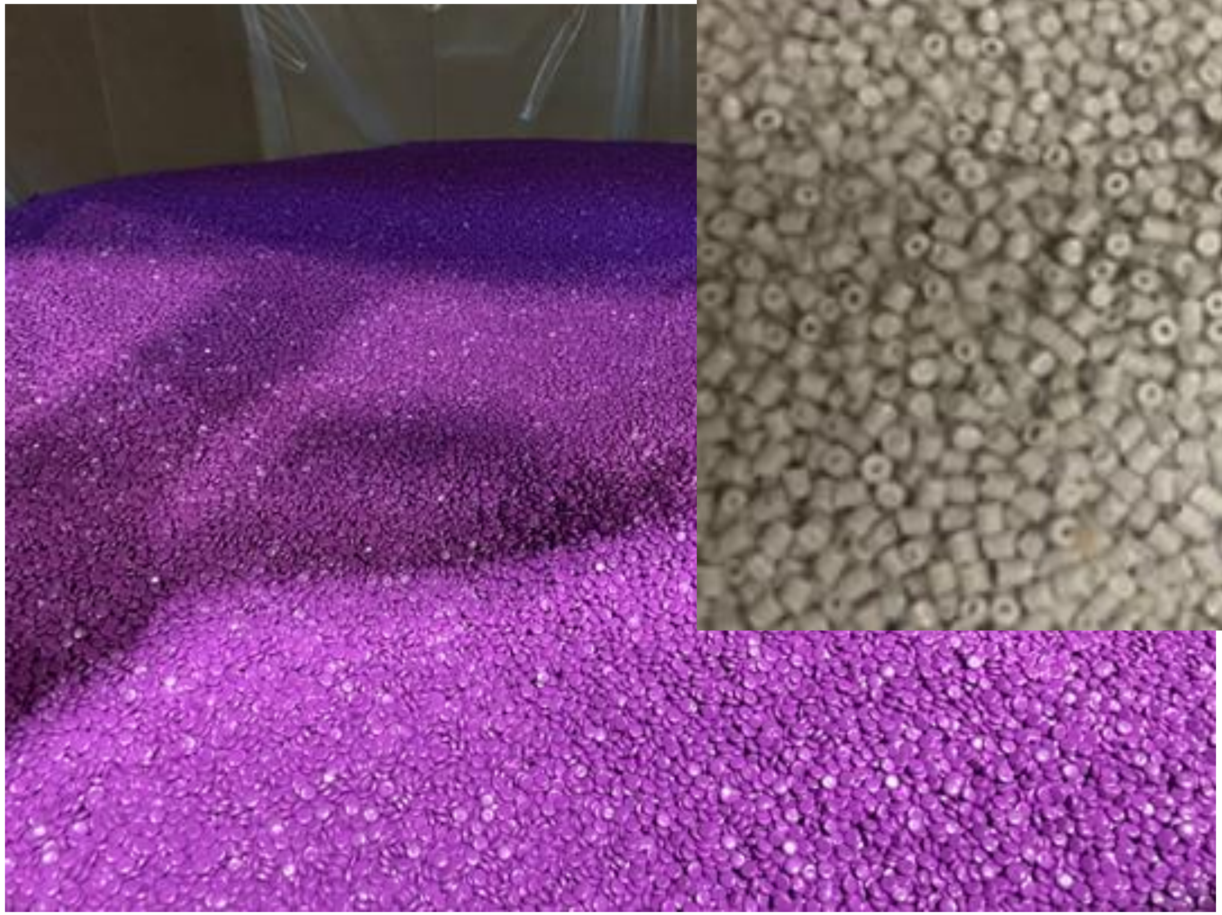
Project methodology

- Different recycling sources are tested, the recyclates are characterized (TGA, DSC, OIT, MVR, mechanical properties).
- The formulations are chosen regarding a possible application for the used recyclates.
- Within the project PP-, PE-, PA6-, PA66-, PET- and PC/ABS-recyclates are evaluated.
- The flame retarded recyclates will be tested for their thermal stability in an oven aging under application specific settings (1000 – 2000 h at up to 150 °C).



  Open

Fraunhofer LBF



Polypropylene

Polypropylene
Recyclate characterization

PIR-PP1

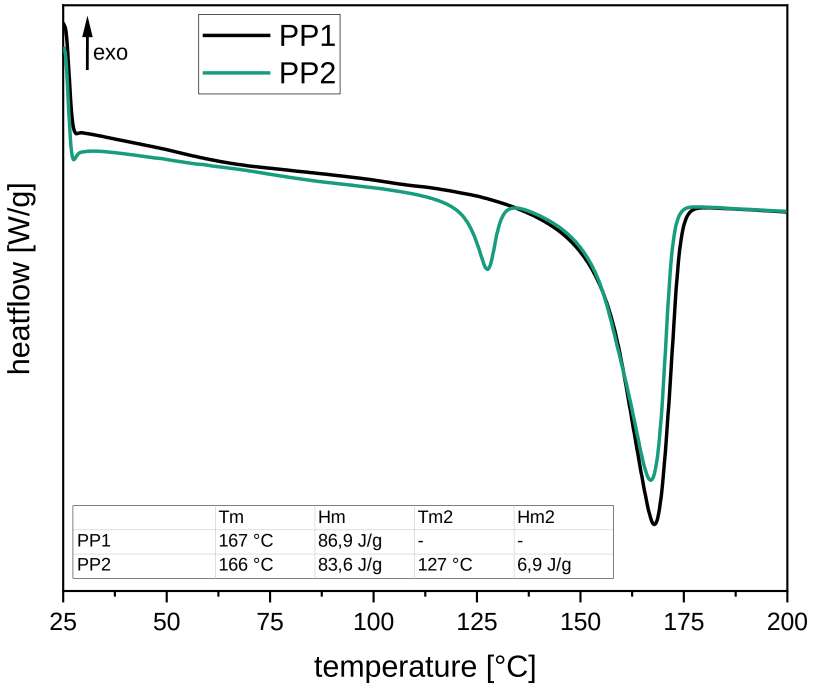
Colour: Purple
Odor: no smell noticed

MVR (230°C/2,16 kg): 3.7 g/10 min

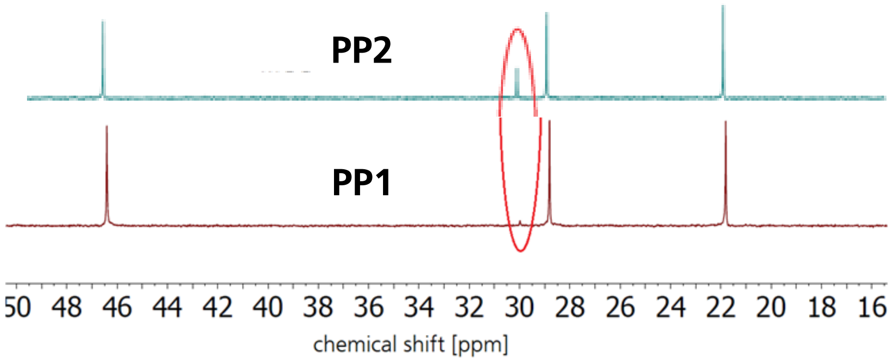
OIT (220 °C): 7 minutes

DSC measurements were performed under nitrogen atmosphere with a heating rate of 10 K/min over a temperature range of 25°C to 200°C

PE-Impurity: 2 % (via NMR)



	Tm	Hm	Tm2	Hm2
PP1	167 °C	86,9 J/g	-	-
PP2	166 °C	83,6 J/g	127 °C	6,9 J/g



PCR-PP2

Colour: light grey
Odor: no smell noticed

MVR (230°C/2,16 kg): 10 g/10 min

OIT (220 °C): 2 minutes

DSC measurements were performed under nitrogen atmosphere with a heating rate of 10 K/min over a temperature range of 25°C to 200°C: shows PE peak at 127 °C.

PE-Impurity: 12 % (via NMR)

  Open

Polypropylene

Performance in flame retardancy

PIR-PP1

Flame retardant: FR1-P

UL 94V:
- Secure V0 classificaion @3.2 mm
- Between V0 and V2 @1.6 mm

After Aging at 135 °C flame retardancy @3.2 mm was stable over 40 days.

After aging at 135 °C at cone calorimetry shows a stable TTI and TTB, pHRR, THR and MARHE.

GWFI @850 °C is stable aster aging at 140 °C for 40 days.

Both PP recyclates show specific properties that need to be dealt with, the performance of the mechanical propertie and flame retardancy aligns with the product specifications!

PCR-PP2

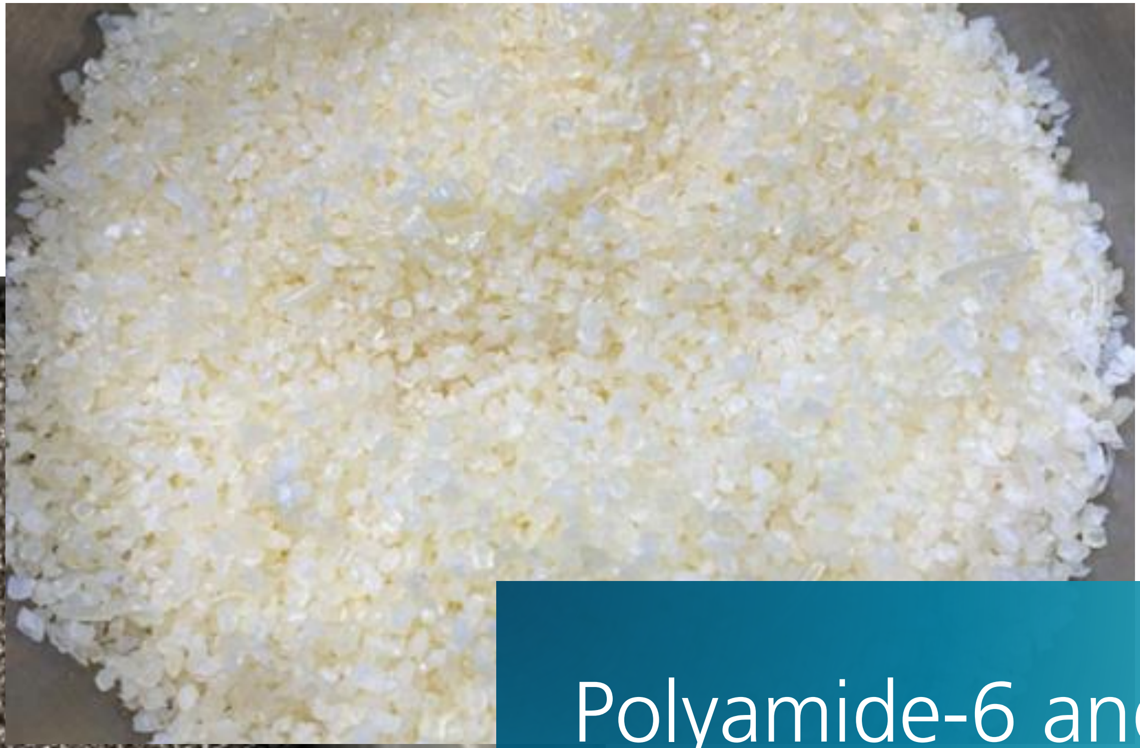
Flame retardant: FR1-P

UL 94V:
- Secure V0 classificaion @3.2 mm
- Stable V0 classification @1.6 mm

After aging at 135 °C flame retardancy was stable over 40 days.

After aging at 135 °C at cone calorimetry shows a stable TTI and TTB, while increasing pHRR, THR and MARHE.

GWFI @850 °C is stable after aging at 140 °C for 40 days.



Polyamide-6 and -66 with glass fiber

Polyamide with glass fiber

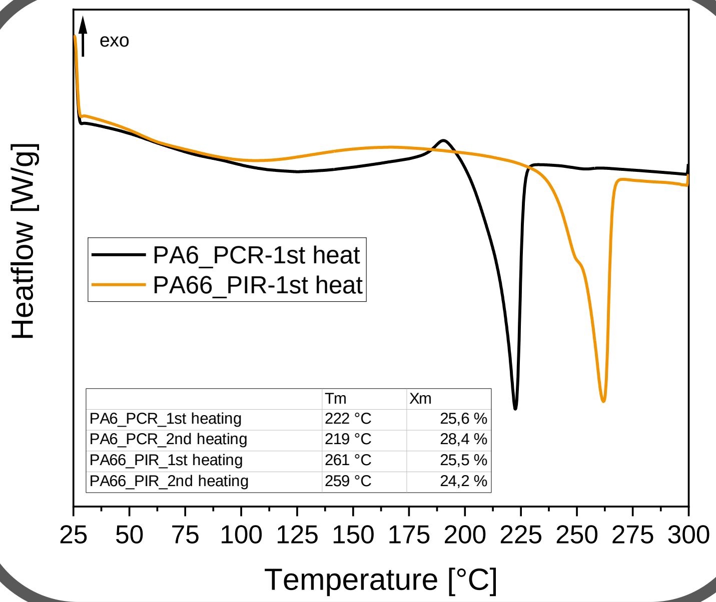
Material characterization

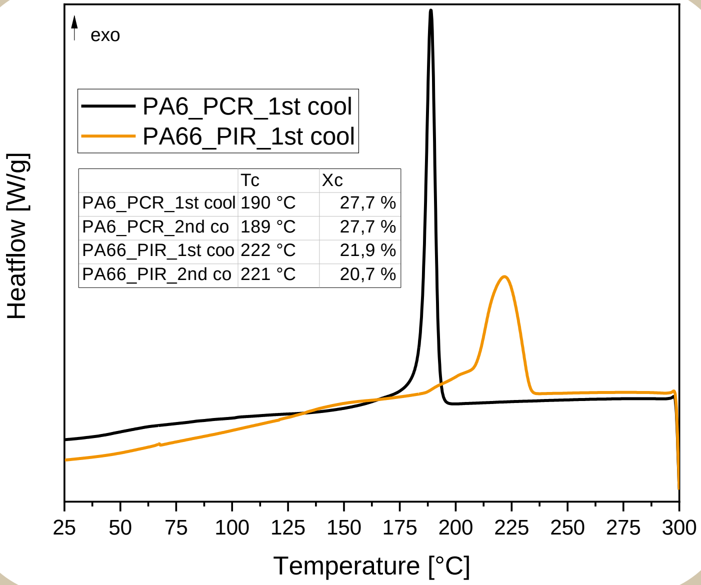
PCR-PA6

Colour: black
Odor: no smell noticed

MVR measurements (250°C / 2.16 kg): 30.4 cm³/10 min

DSC measurements were performed under nitrogen atmosphere with a heating rate of 10 K/min over a temperature range of 25°C to 300°C





PIR-PA66

Colour: nature
Odor: no smell noticed

MVR measurements (275°C / 2.16 kg): 77.2 cm³/10 min

DSC measurements were performed under nitrogen atmosphere with a heating rate of 10 K/min over a temperature range of 25°C to 300°C

Polyamide with glass fiber

Performance in flame retardancy

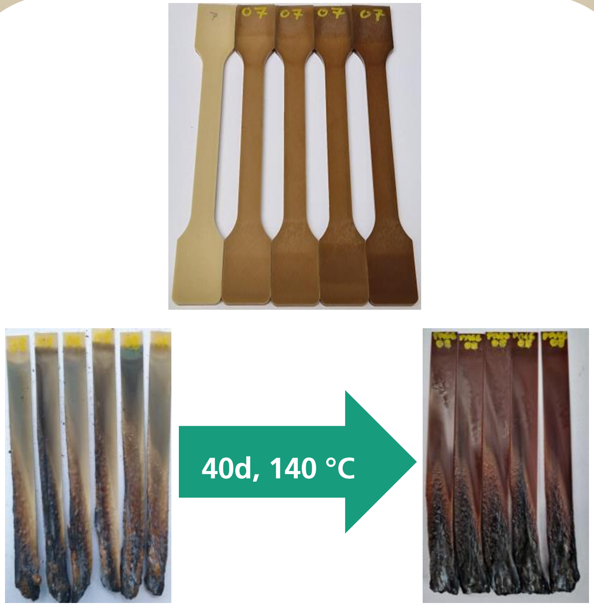
PCR-PA6

30% glass fiber
FR2-P-N

Stable V-0 classification @1.6 mm and @3.2 mm. Also after 40 days @140 °C.

GWIT is passed at 750 °C and up to 800 °C after thermal aging.
GWFI is measured at 960 °C.
CTI is passed at 600 V and slighty decreases after aging

FR3-P-I-N gives also a stable V-0.
Even increases the GWIT to 775 °C.



PIR-PA66

25% glass fiber
FR2-P-N

Stable V-0 classification @0.8, @ 1.6 and @3.2 mm. The classification is also passed after 40 days @140 °C.

GWIT is passed constant at 800 °C and GWFI is passed at 960 °C before and after thermal aging.
CTI is passed at 540 V and stays stable after aging.

FR3-P-I-N gives also a stable V-0 and even increases the CTI to 600 V.

  Open

Fraunhofer LBF

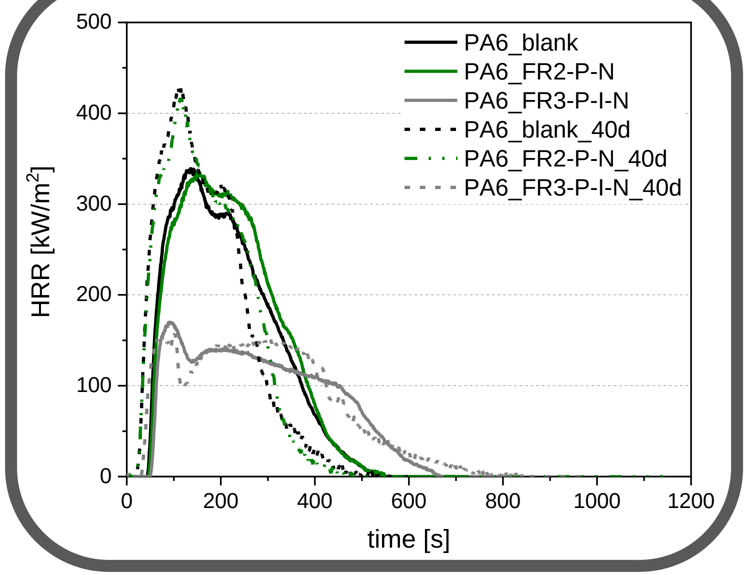
Polyamide with glass fiber
Performance in flame retardancy

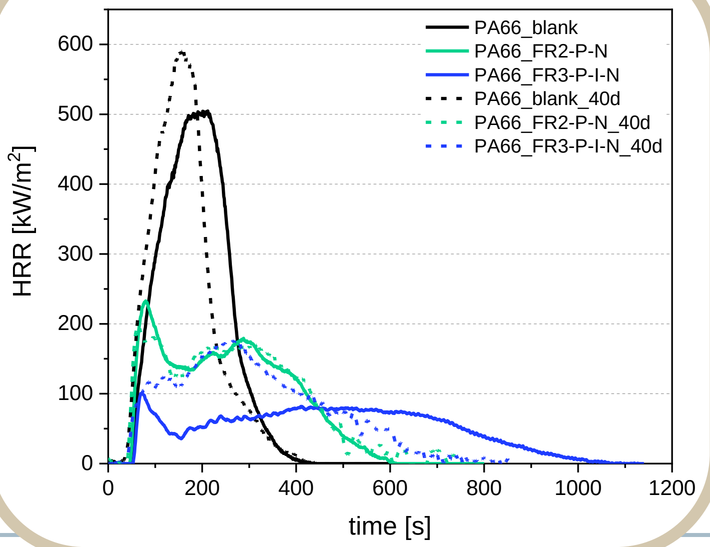
PCR-PA6
30% glass fiber
FR2-P-N

Cone Calorimetry

	blank	FR2-P-N	FR3-P-I-N
TTI	42 s	43 s	54 s
TTB	526 s	605 s	681 s
pHRR	362 kW/m²	184 kW/m²	162 kW/m²
THR	85.3 mJ/m²	66.2 mJ/m²	58.5 mJ/m²
MARHE	241 kW/m²	141 kW/m²	110 kW/m²

After aging at 140 °C for 40 days the measured metrics stay almost constant, except for the FR3-P-I-N system, where the TTI is reduced .





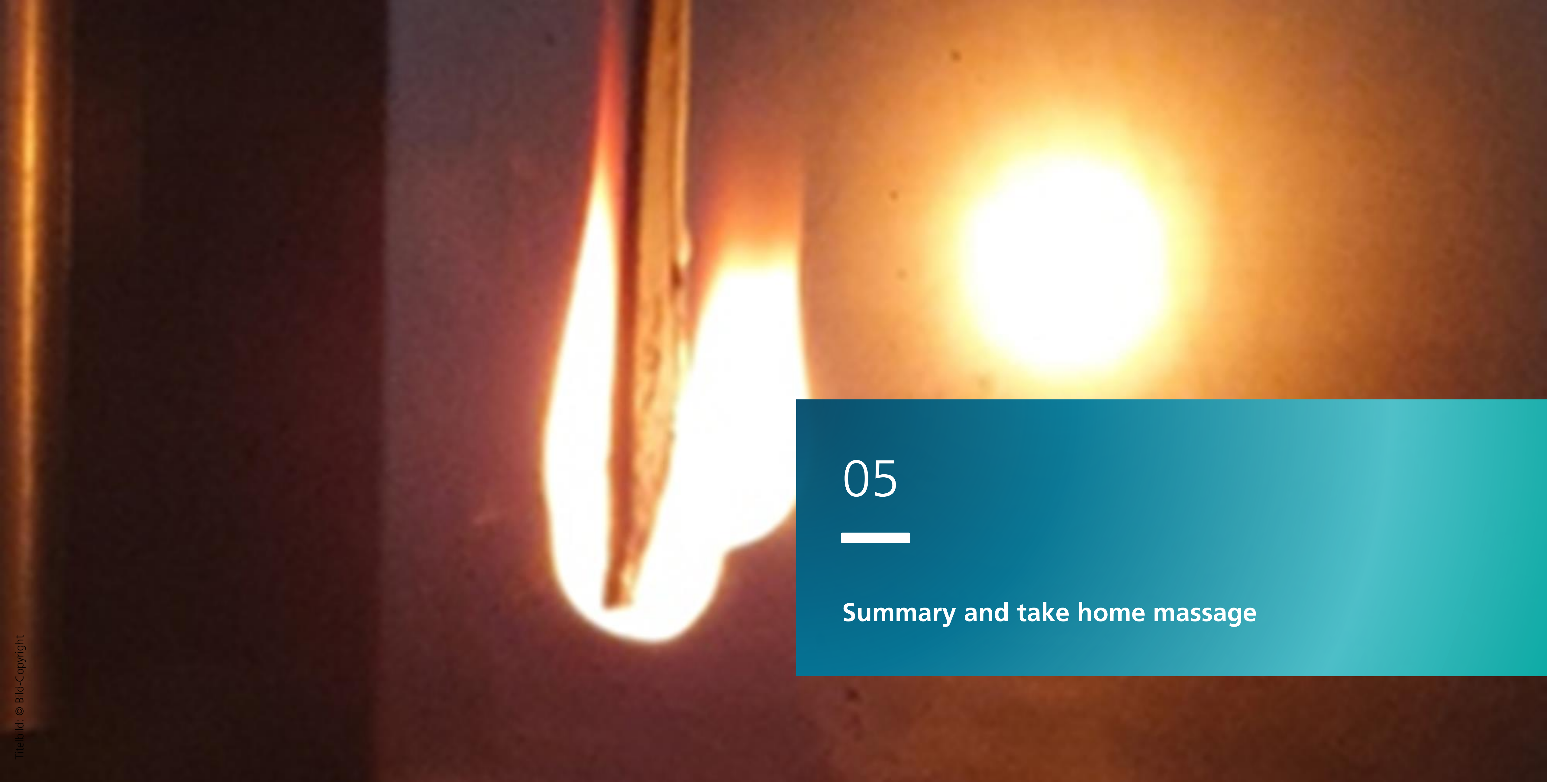
PIR-PA66

25% glass fiber
FR2-P-N

Cone Calorimetry

	blank	FR2-P-N	FR3-P-I-N
TTI	49 s	52 s	48 s
TTB	431 s	972 s	1013 s
pHRR	505 kW/m²	107 kW/m²	109 kW/m²
THR	88.9 mJ/m²	60.8 mJ/m²	57.9 mJ/m²
MARHE	300 kW/m²	77.2 kW/m²	72.6 kW/m²

After aging at 140 °C for 40 days the measured metrics stay almost constant.



05

Summary and take home massage

Fraunhofer LBF

Summary and take home massage

What did we learn?

- Market available recyclates need a defined characterization with common methods.
- In General typical flame retardant formulations for specific applications work in recyclates, but for the use in long-term applications the material properties need to be adjusted by re-additivation (depending on the residual stabilization and impurities).
- Evaluate which material flows are suitable for upcycling and how big is influence of the recyclate quality on the performance of the flame retardant.
- It is possible to fit formulations based on recyclates on current material specifications, but the variation of the material properties can be higher, i.e. for PCRs. Specifications probably need to be adjusted!

- To get a deeper knowledge into the categorization and analyzation of waste streams a broughter study needs to be carried out.
- What happens when materials come back from closed loop systems, probably after a long usage time?
- A lot of topics regarding, interactions between additives, FRs, fillers are still unknown and will be handled in future projects. Very complex questions, that need more cooperation between all players alon the product chain!
- **The time to act is know, Reach out to us and our partners to cooperate in the future!**

Project Partners: Thank you!

Budenheim

ICL

RADICI GROUP

CLARIANT

MGG POLYMERS

SÜDPACK

HUBER ADVANCED MATERIALS

Nabaltec

Schneider Electric

THOR

Dr. Michael Großhauser

Fraunhofer LBF

phone +49 6151 705 – 8757

michael.grosshauser@lbf.fraunhofer.de

Open

Fraunhofer LBF