Solid-state polymerization on degraded PHBV: An effective and eco-friendly alternative for biopolymer valorization.

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Introduction

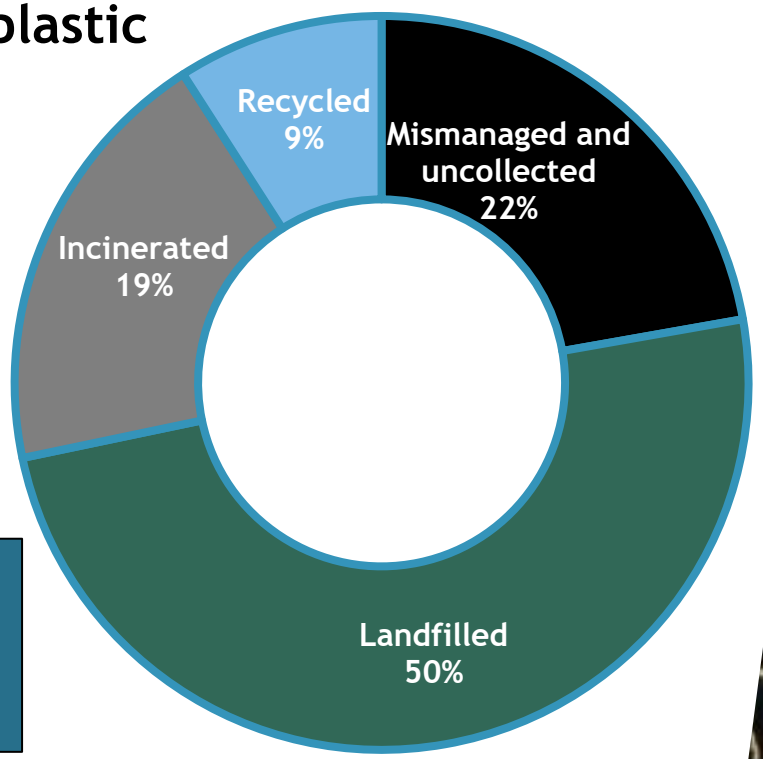
Plastics context

Conventional polymers

Most of all the plastic produced worldwide (2021).

- Toxic additives and microplastic
- Petroleum-derived
- Extremely durable

POLYMERS END-OF-LIFE (2019)



Source: OECD Global Plastics Outlook Database

Biodegradable biobased polymers

❖ Part of the solution

- From renewable resources
- Reduce carbon footprint

Consider end-of-live scenario

Biodegradable biobased polymers

Candidates

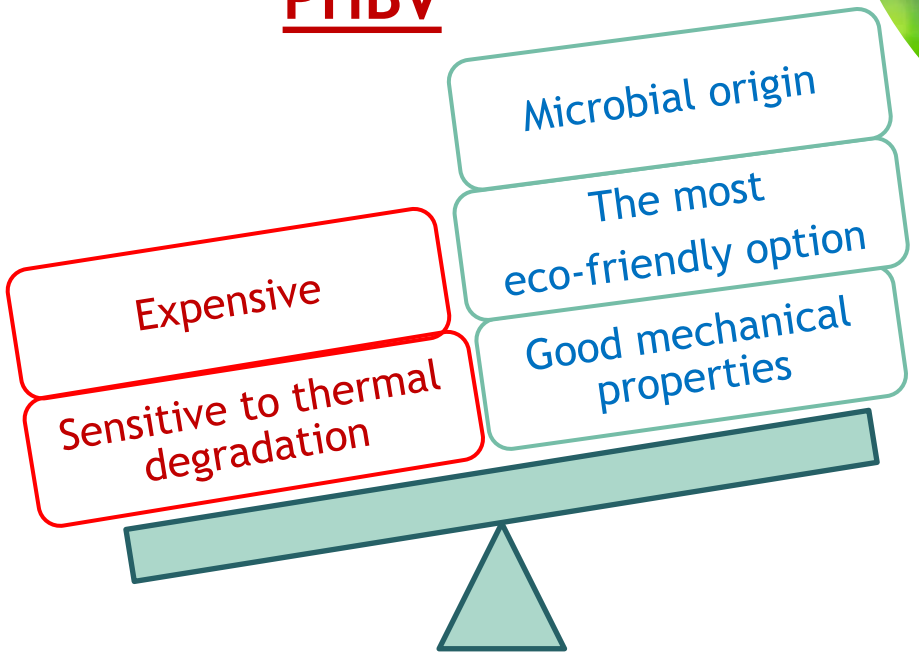
- **PLA**
  Poly(lactic acid)
- **PHBV**
  Poly(hydroxybutyrate-co-hydroxyvalerate)
- **Others (thermoplastic starch…)**

Expensive

VALORIZATION

- Composting
- Energy recovery
- Chemical recycling
- ***Mechanical recycling***

PHBV



MECHANICAL RECYCLING

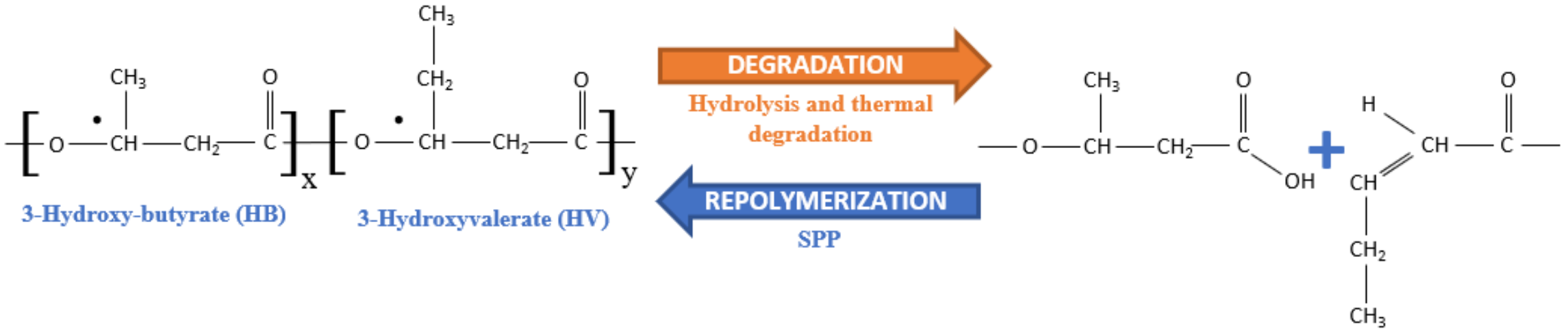
Decrease final product properties

Solid state polymerization (SSP)

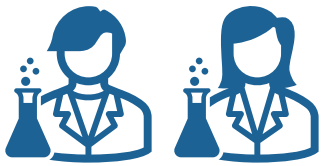
- Cheap
- No additives
- Eco-friendly

Low heating
+
Vacuum

PHBV

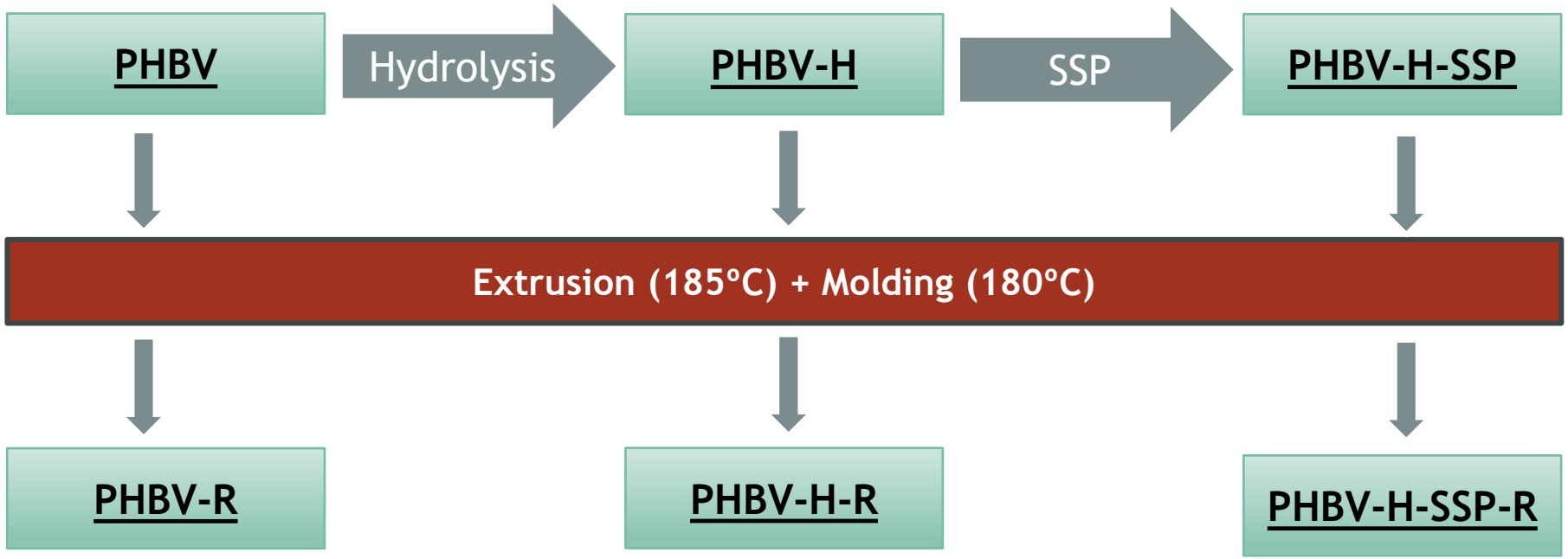


SSP can revert degradation? → Let test



Methodology

PHBV-SSP: PROCEDURE



Main goals:

- Effect of hydrolysis.
- Effect of SSP.
- Effect of thermal degradation during mechanical processing.

Results and discussion

Hydrolysis effect

Intrinsic viscosity (μ):

- μ ↓ 65 % after 4 days hydrolysis.
- μ ↑ 30 % after SSP.

✓ SSP effectivity in highly degraded PHBV

Agrees GPC results ⟶ Average molecular weight (MW)

Hydrolysis effect

Intrinsic viscosity and molecular weight

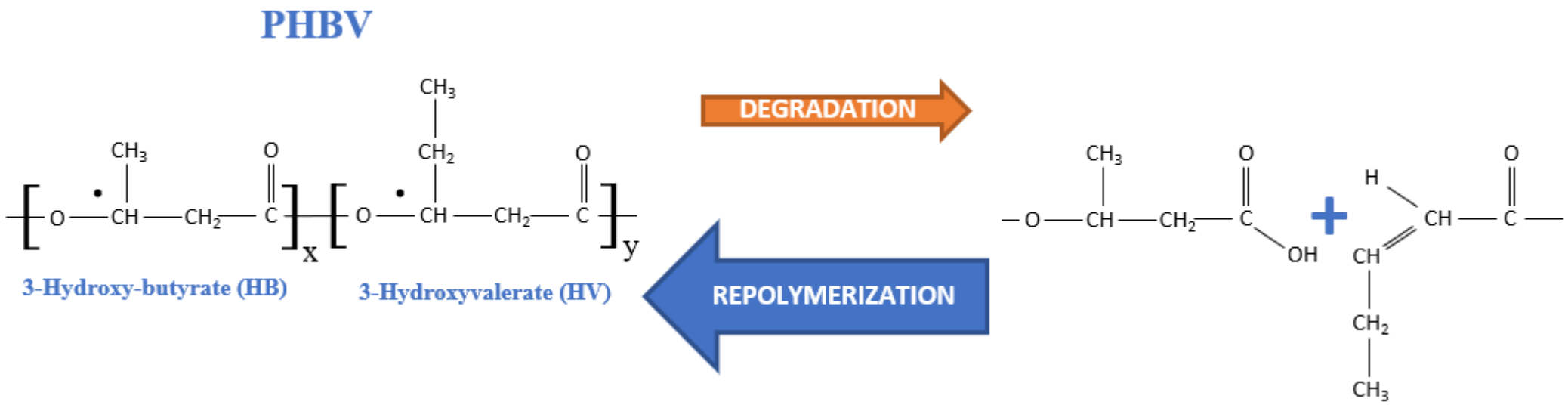
Hydrolysis

4 h	1 day	3 days	4 days
≈	↓ 20 %	↓ 50 %	↓ 65%

Chain braking → ↓ Average molecular weight

↓ Viscosity

Solid state polymerization (SSP)



SSP effectivity

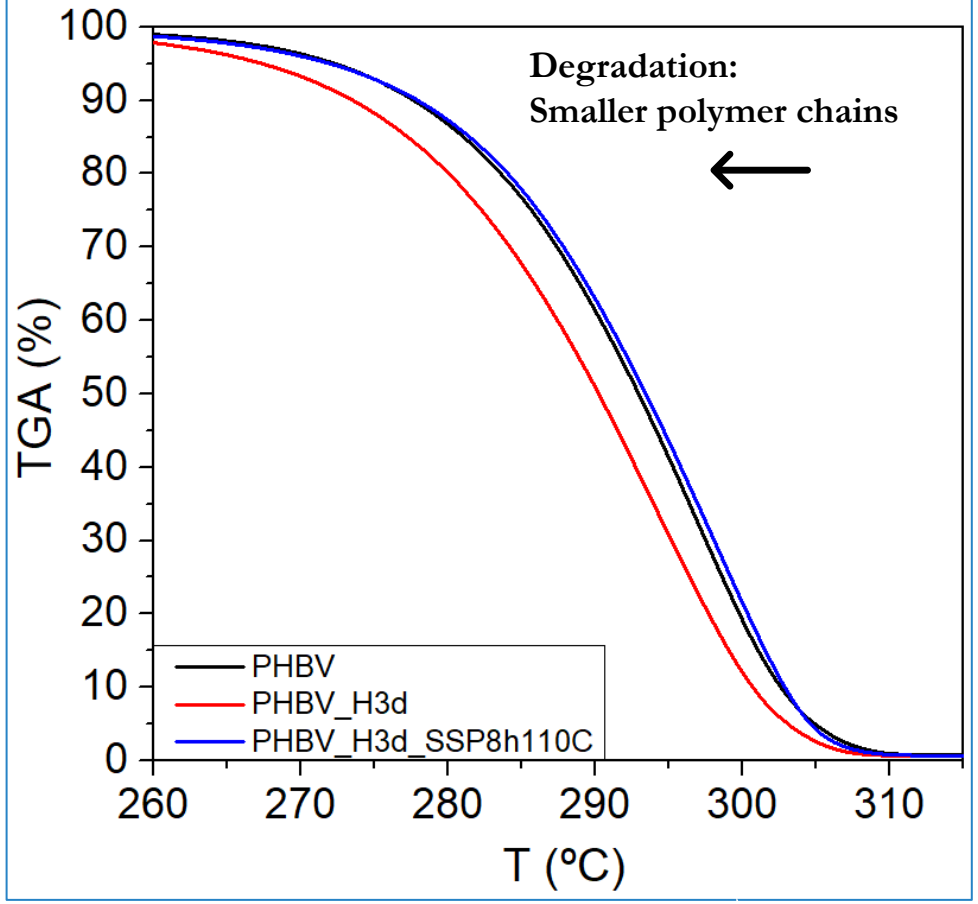
- Operation time
- Temperature
- Degradation level of the samples

Optimum conditions:

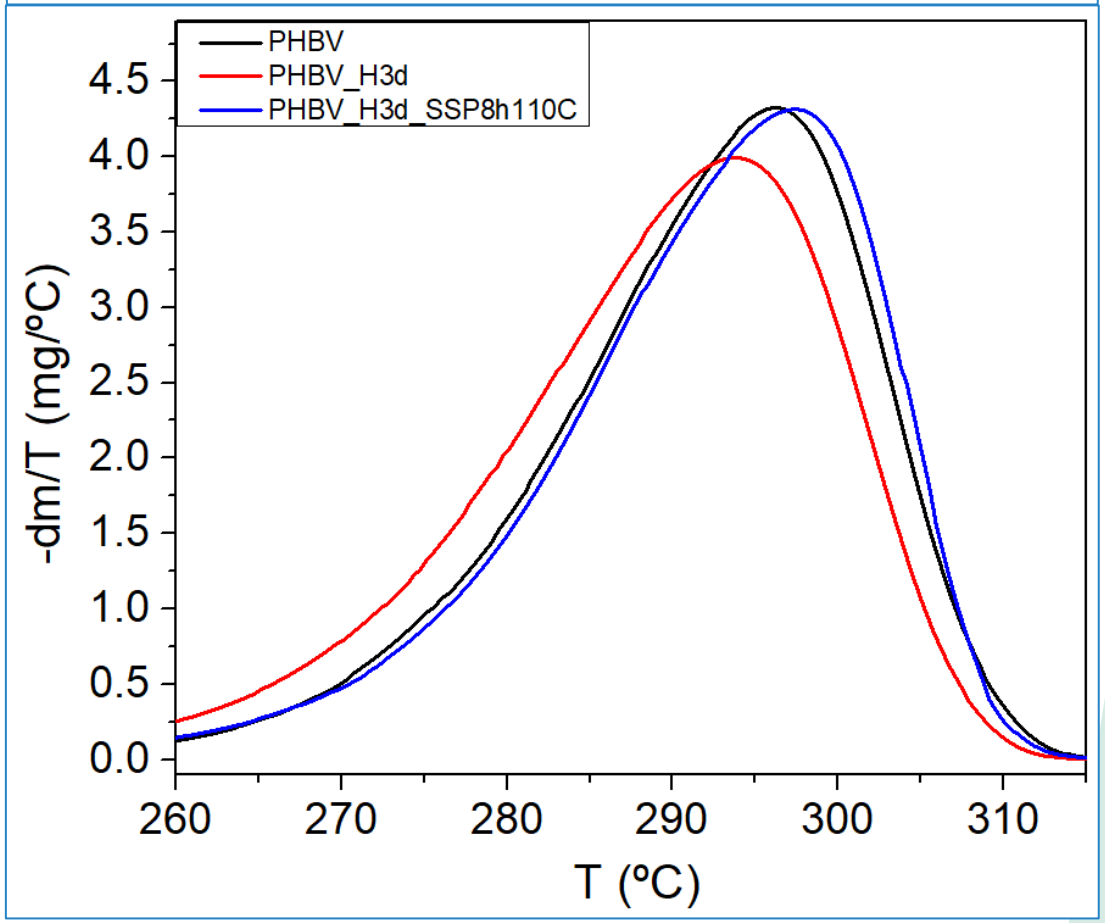
Degradation	μ and MW
Slight	↑ 15 % ✗
Moderate	↑ 60 % ✓

TGA: Hydrolysis and SSP effect

TGA



DTG



SSP → **Reverse the degradation effect** ✓

Mechanical recycling effect

Intrinsic viscosity and molecular weight

Extrusion (185 ºC) + Molding (180 ºC)

Virgin	After hydrolysis	After SSP
↓ 45 %	70 % ↓	↓ 55 %

↑ **Thermal degradation degree**

SSP ↑ 15 % viscosity and molecular weight

✓ A better final product

Conclusions

- Hydrolysis and reprocessing decrease viscosity, molecular weight and PHBV properties
- SSP increase viscosity and molecular weight of degraded PHBV.
- SSP is effective for highly and moderate degraded PHBV samples.
- SSP is an outstanding, effective and simple way to valorise degraded PHBV samples.

THANKS FOR YOUR ATTENTION