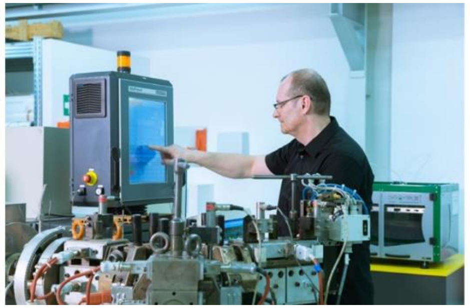
KUNSTSTOFF TECHNIK LEOBEN

KUNSTSTOFFVERARBEITUNG



Polyhydroxybutyrates for a Circular Economy: Mechanical and Thermal Characterization

Priyanka Main

06.09.2022

2nd International Symposium on Plastics Technology

Aachen

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 859885.

C-PlaNeT

CIRCULAR PLASTICS NETWORK FOR TRAINING

Contents

- Bioplastics
- PHB
- Mechanical Recycling Pathway
- Mechanical Properties
- Thermal Properties
- Summary

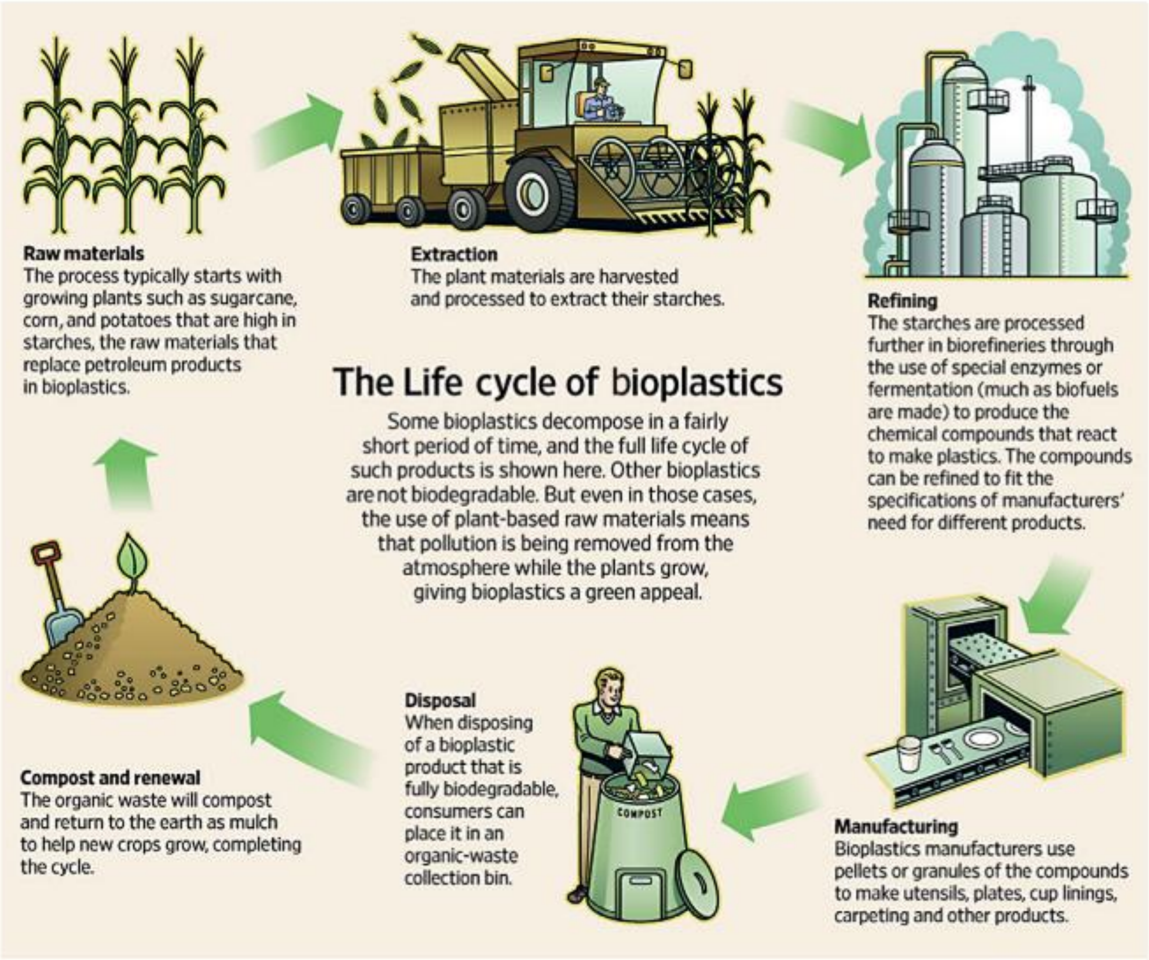


Fig.1:The life cycle of bioplastics. CTC Clean Tech Consulting GmbH; WSJ reporting.
Ashter, S.A.: Introduction to Bioplastics Engineering, PDL handbook series, Elsevier, 2016

Bioplastics

Need for Bioplastics

- Packaging is the biggest application of all the plastics produced(39.5%).
- In 2020, 29.5Mt of plastic post consumer waste was collected out of which 61% was packaging waste.
  - 46% of the packaging waste was sent to recycling (8.2Mt)
- Out of 4.6Mt of post consumer recycled plastic produced- 30% is used in packaging
- But it still only accounts for 6.6% recycled content rate in making packaging.
- Progress is being made, but to reach the EU policy targets: biobased feedstock need to be explored further along with mechanical recycling as an EoL option.[1]

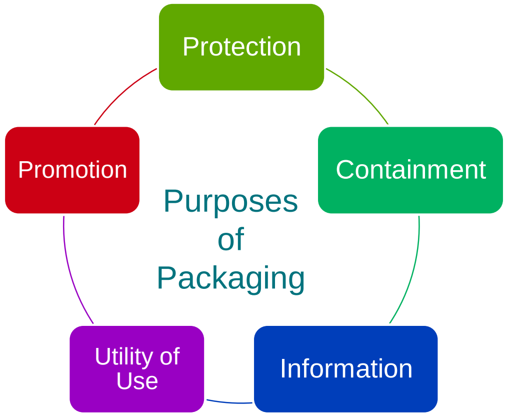


Fig.2: The 5 purposes of packaging

Advantages

Replace

Reduce fossil fuel dependency by using renewable resources, replacing existing plastics with bio-based counterparts (e.g., drop-in plastics)

Reduce

Potential environmental benefits in terms of GWP reduction

Simplifies

The use of compostable plastics, in applications where organic contamination is expected, simplifies waste management and returns carbon to soil as compost

Contribute

Anaerobic digestion of biodegradable plastics can produce large specific energy and contribute to achieve an optimal ratio of carbon to nitrogen in the process

Mitigate

Biodegradable plastics could replace non-degradable plastics in products that are likely to leak in the environment, potentially mitigating plastic pollution

[2]

Disadvantages of Bioplastics

Ethics

Using first-generation biomass, which is often edible, remains controversial owing to potential competition with food production. Processes to efficiently use second-generation biowastes need to be established.

Efficiency

Bioplastic manufacturing processes can be less energy efficient than fossil-based plastic processes and come with other environmental burdens associated with agricultural farming.

Economics

Most bioplastics are currently more expensive to produce than fossil-based plastics, mostly owing to economies of scale and the price competitiveness of crude oil.

End of life

For most bioplastics, recycling streams have yet to be established to make them truly 'circular'. Consumers remain uncertain of how to deal with bioplastics after use. Compostable bioplastics are often rejected by composters.

Education

Consumers and plastic converters are confused about the usefulness of bioplastics, owing to inconsistent labelling, contradicting life cycle assessments and 'greenwashing'. Improved information distribution and consistent global standards need to be established

[3]

PHAs

PHAs

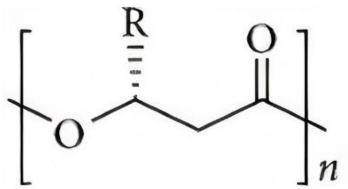
- Polyhydroxyalkanoates
- PH3B- Polyhydroxybutyrate
- Biobased and biodegradable
- Polyesters
- Produced by- microorganisms

in different conditions.

- Accumulated as intracellular storage

granules.[4]

- The general structure:



[5]

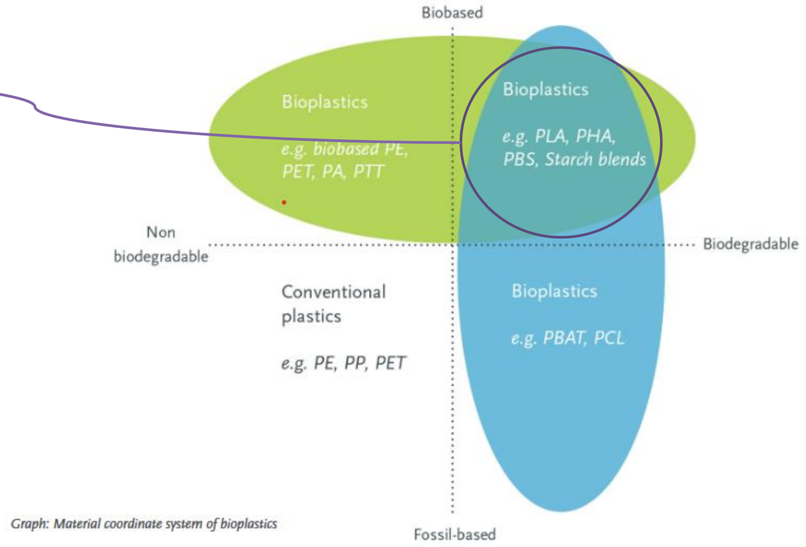
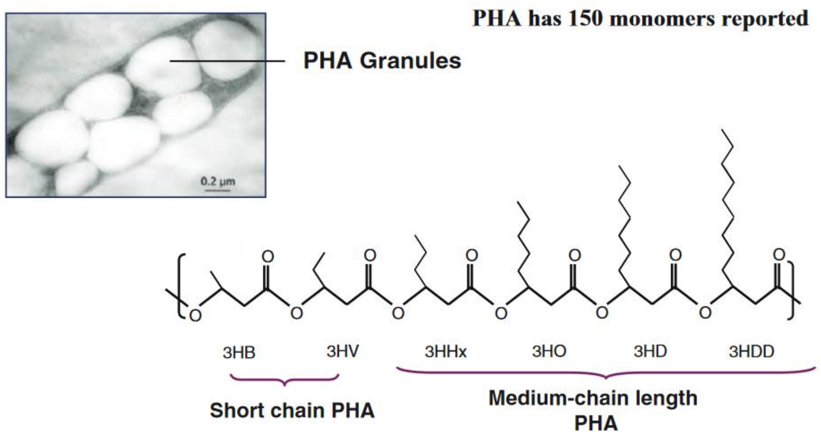


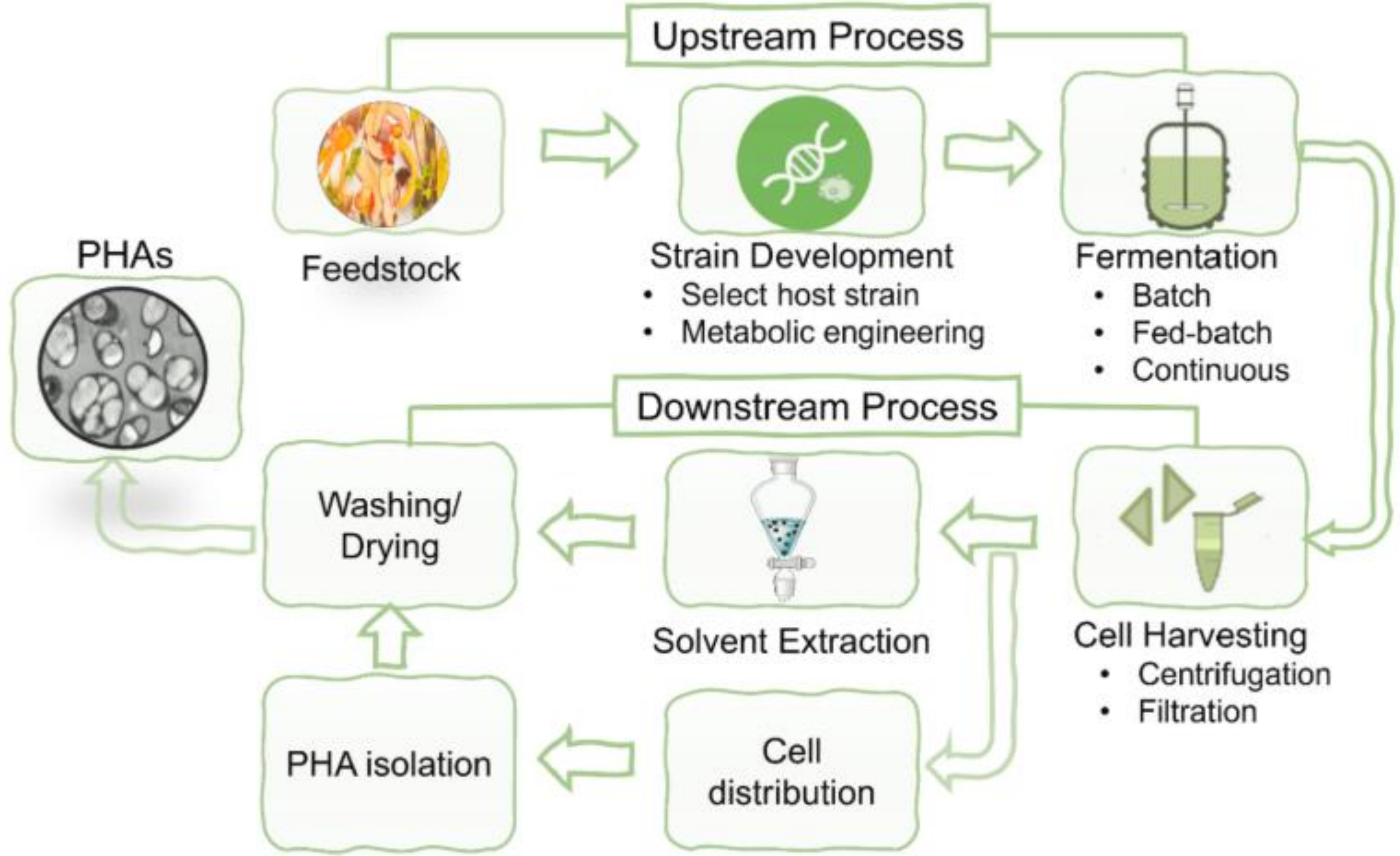
Fig.3:European Bioplastics: What are bioplastics?, Fact Sheet



[6]

Common PHA monomers

Production



[7]

PHB properties

- PHB is characterized by having
  - a methyl functional group (CH_3) and
  - an ester linkage group (−COOR)

Table 1. Summary of mechanical properties of P3(HB) and petrochemical based (PP, PET, PE) and bio-based polymers (PLA).

Mechanical Property	P3HB	PP	PET	LDPE	HDPE	PLLA	PDLLA
Tensile modulus (GPa)	3–3.5	1.95	9.35	0.26–0.5	0.5–1.1	2.7–4.14	1–3.45
Tensile Strength (MPa)	20–40	31–45	62	30	30–40	15.5–150	27.6–50
Elongation at break (%)	5–10	50–145	230	200–600	500–700	20–30	1.5–20
Degree of Crystallinity (%)	50–60	42.6–58.1	7.97	25–50	60–80	13.94	3.5
Melting Temperature (°C)	165–175	160–169.1	260	115	135	170–200	amorphous
Glass Transition Temperature (°C)	5–9	−20–−5	67–81	−130–100	−130–100	50–60	50–60

- Thermoplastic, hydrophobic, high crystallinity, and brittle characteristics.[5]
- In terms of molecular weight, melting point, crystallinity and tensile strength, PHB is still equivalent in comparison with a conventional plastic of polypropylene (PP).
- It is even better than PP and PET with respect to oxygen, water vapor, fat and odour barrier properties. Therefore, a development of PHB mechanical properties is necessary to fully exploit its useful attributes for packaging applications [8]

Crystallization aspects

- Perfect isotactic structure of the polymer chains, with all chiral carbon atoms in (R)-configuration

- Spherulites- PHB forms aggregates of lamellae, most commonly of a spherical shape.
- Does not contain foreign particles that may act as heterogeneous nucleation sites.
  - **low nucleation density** compared to most polymers
  - **extremely large spherulites** formed (few mm, or even cm)

- When PHB spherulites are cooled to room temperature:
  - radial cracks departing from the spherulite centers,
  - circumferential cracks around spherulites [9].

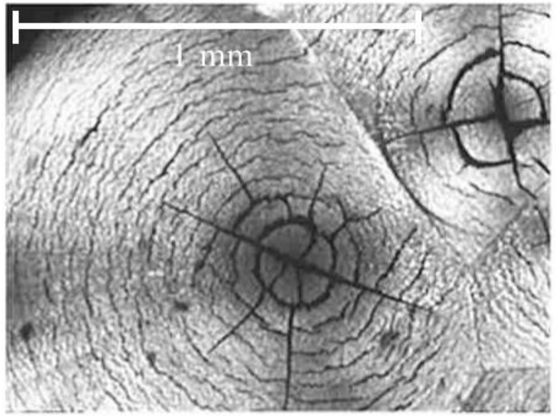


Fig. 4: POM micrograph of a PHB film, crystallized during cooling at 5 K/min, after prior melting at 200C for 3 min.

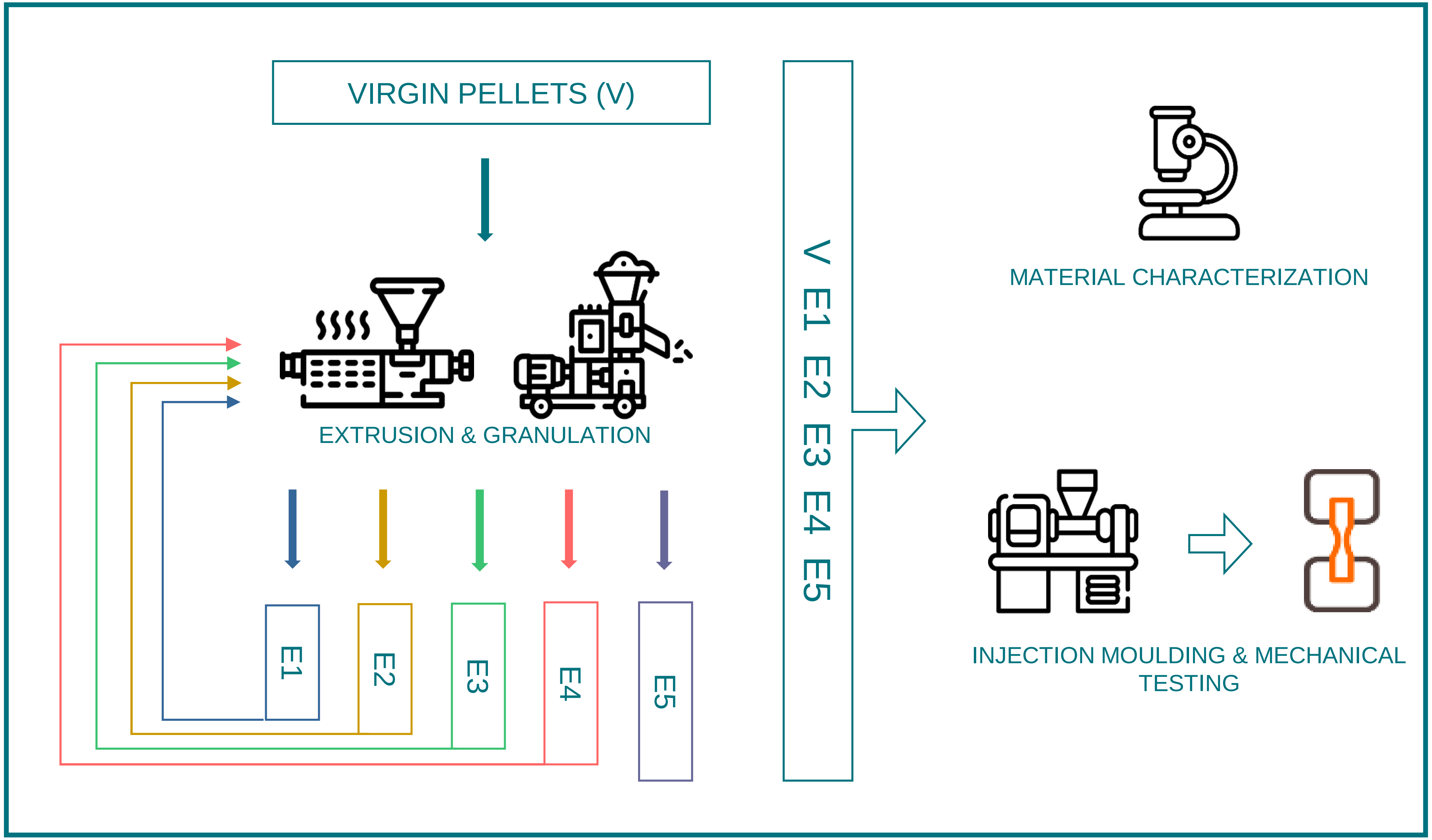
- Crystallization from melt is slow, in the form of large spherulites, whose size can be decreased using nucleating agents [4].

Challenges

- Narrow processability window
  - resulting in this material being susceptible to thermal degradation at temperatures in the region of the melting point.
- In general,
  - polymers with a low degree of crystallinity have been found to demonstrate a wider processing window,
  - polymers with a higher degree of crystallinity usually showed a narrow window, due to a sharper melting range.
- Soon after the PHB materials are produced,
  - they can undergo slow changes in their amorphous and crystalline properties, resulting in the hardening or weakening of the material.
  - This process is more commonly referred to as the aging of PHB and its nature derives from two phenomena:
    - the secondary crystallization and the physical aging [5]

Recycling

Mechanical Recycling Pathway



Mechanical Properties

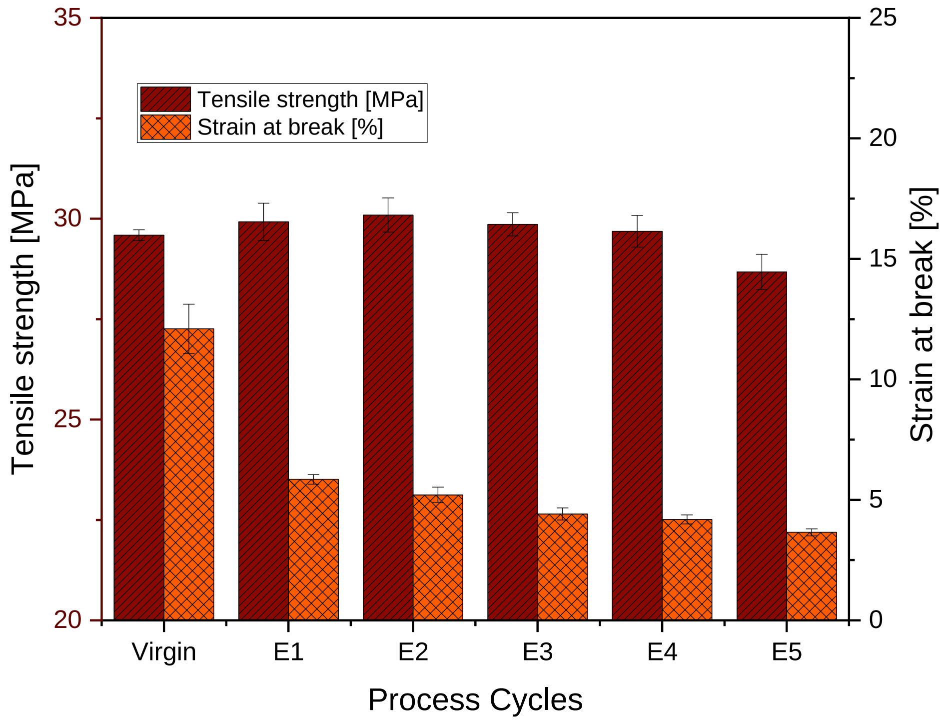


Fig 5. : Tensile strength and Strain at Break vs. Process Cycles

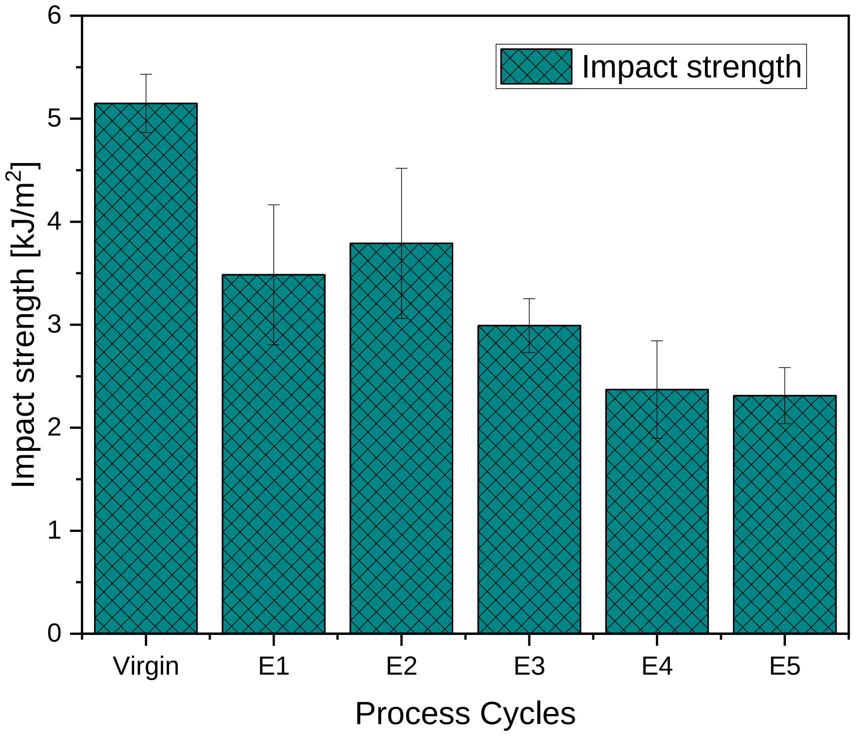


Fig. 6: Impact Strength vs. Process Cycles

Main points:

- Tensile strength remains mostly constant till E4 with a slight drop at E5.
- Strain at Break decrease observed with 50% drop in Virgin to E1 itself.
- Charpy Notched Impact strength corroborated the strain at break results by the progressive brittleness of the samples with a 50% reduction at the end of E5.

Thermal Properties

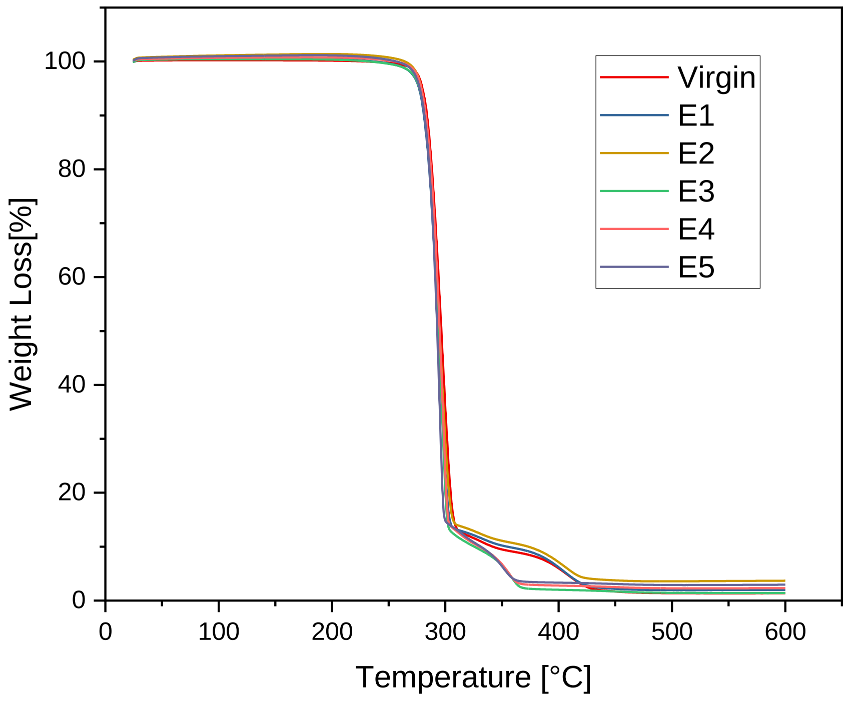


Fig.7 TGA of PHB Virgin, E1-E5

- DSC- The degree of crystallinity from the 1st heating scan of the materials marginally increased as the cycles progressed from 40% to ~47%.
- The melting temperature did not vary a lot with each cycle and was ~177°C.
- TGA-The thermal stability of the material was assured by only marginal changes in the degradation temperature in the 5 processing cycles.
- Moraczewski observed a similar result and stated that as the degree of crystallinity increases so does the thermal stability (Moraczewski, 2016).

Summary

- Biopolymers are increasing in the market.
- PHB is an interesting bioplastic but with some challenges.
- Circular Economy potential- mechanical recycling of PHB objective.
- Reprocessing +injection moulding- mechanical and thermal characterization.
- Tensile strength remained mostly constant.
- Strain at Break and Charpy Impact Strength showed a decrease as the cycles progressed due to chain scission and increasing degree of crystallinity as observed by DSC analysis.
- Degradation temperature and melting point remained stable for all the cycles. This shows promise for PHB to be mechanically recycled.

References

1. PlasticsEurope: The Circular Economy For Plastics, A European Overview, 2022
2. Di Bartolo, A.; Infurna, G.; Dintcheva, N.T.: A Review of Bioplastics and Their Adoption in the Circular Economy, Polymers 13 (8), 2021
3. Rosenboom, J.-G.; Langer, R.; Traverso, G.: Bioplastics for a circular economy, Nature reviews. Materials, 2022, pp. 1–21
4. Piorkowska, E. (2019). Overview of Biobased Polymers. In M. L. Di Lorenzo & R. Androsch (Eds.), *Advances in Polymer Science: Vol. 283. Thermal Properties of Bio-based Polymers* (Vol. 283, pp. 1–35). Springer
5. McAdam, B.; Brennan Fournet, M.; McDonald, P.; Mojicevic, M.: Production of Polyhydroxybutyrate (PHB) and Factors Impacting Its Chemical and Mechanical Characteristics, Polymers 12 (12), 2020
6. Chen, G.-Q.: Plastics Completely Synthesized by Bacteria: Polyhydroxyalkanoates, In: Chen G.G.-Q. (Ed.): Plastics from Bacteria, Microbiology Monographs, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, pp. 17–37
7. Muthuraj, R.; Valerio, O.; Mekonnen, T.H.: Recent developments in short- and medium-chain- length Polyhydroxyalkanoates: Production, properties, and applications, International journal of biological macromolecules 187, 2021, pp. 422–440
8. Vu, D. H., Åkesson, D., Taherzadeh, M. J., & Ferreira, J. A. (2020). Recycling strategies for polyhydroxyalkanoate-based waste materials: An overview. *Bioresource Technology*, *298*, 122393.
9. Di Lorenzo, M. L., & Androsch, R. (2019). Crystallization of Poly[(R)-3-hydroxybutyrate]. In M. L. Di Lorenzo & R. Androsch (Eds.), *Advances in Polymer Science. Thermal Properties of Bio-based Polymers* (Vol. 283, pp. 119–142). Springer International Publishing.

Priyanka Main
PhD Researcher

priyanka.main@unileoben.ac.at

www.kunststofftechnik.at

Department Polymer Engineering and Science

Chair of Polymer Processing

Montanuniversitaet Leoben

Otto Gloeckel-Strasse 2

8700 Leoben, AUSTRIA

Thank you for your attention!