



BIO-BASED INDUSTRIES
Joint Undertaking
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PHA extrusion

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*BioBarr workshop
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“New bio-based food packaging materials with enhanced barrier properties” (BioBarr)
<http://www.biobarr.eu/>
GA. No. 745586

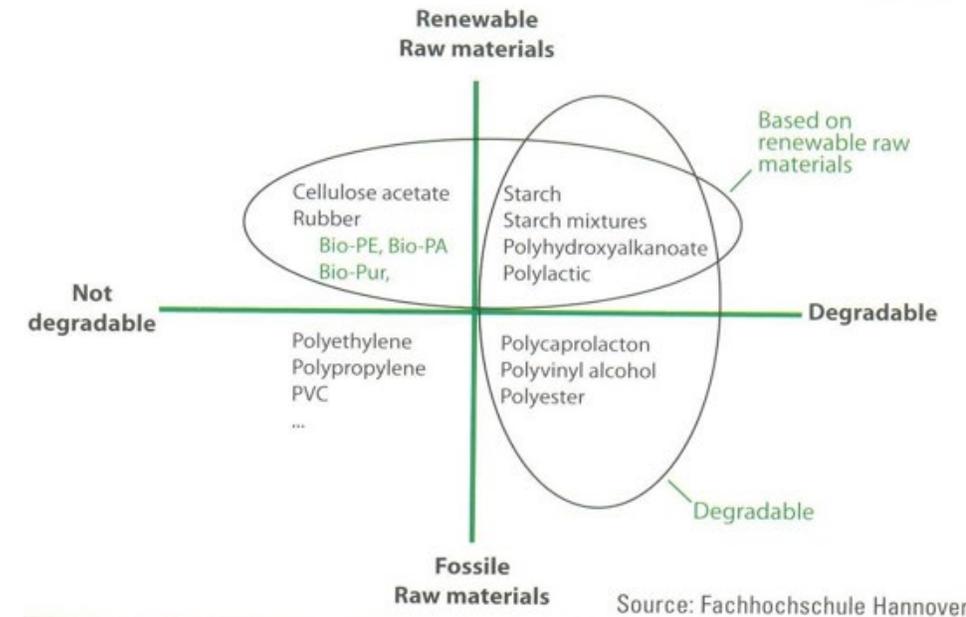


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Biopolymers

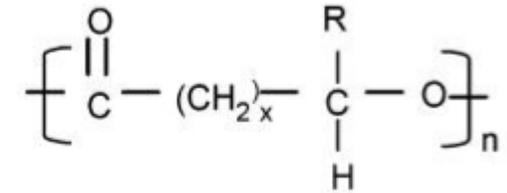
- ▶ Divisions of biopolymers are:
 - ▶ **Bio-based** (from renewal sources) > others (like from fossil based sources)
 - ▶ **Biodegradable** (in nature) > non-biodegradable
- ▶ **PLA** is the most commonly used > **bio-based and compostable** > clear films, rather strong but brittle > moderate barrier properties (WVTR and OTR)
- ▶ **PHAs** are **bio-based and biodegradable** even in seas > **PHB** is brittle but **PHB/V** softer copolymer form > moderate barrier properties but has better WV-barrier than other typical biopolymers
- ▶ **PBS** is a soft polymer and finds usefulness in films due to its polyethylene like processing and properties
- ▶ **Starch-based** thermoplastic blends and formulations > rather weak in barrier especially WV-barrier > composting bags often
- ▶ Biopolymers can be blended together to enhance their processability and/or properties



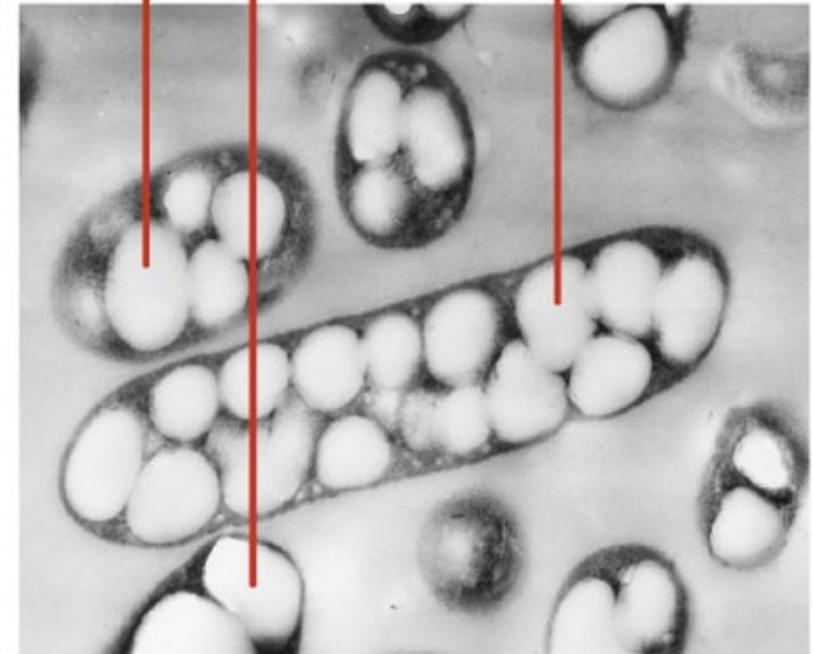
- ❑ PLA, Polylactide, Polylactid acid
- ❑ PHA, Polyhydroxy alcanoate
- ❑ PHB(V), Polyhydroxy butyrate valerate
- ❑ PBS, Polybutylene succinate

PHAs in BioBarr

- ▶ Polyhydroxy alkanates (PHAs) consist of linear polyesters produced by bacterial fermentation of sugar or lipids
- ▶ Typical forms are **polyhydroxy butyrate (PHB)** and **polyhydroxy butyrate-valerate copolymer (PHB/V)**
- ▶ PHB is rather stiff, but it can be softened using valerate (PHB/V)
- ▶ PHAs have rather high melting point (140-180°C) and it resembles PP in properties
- ▶ PHAs are safe to use in packaging and their disposal is easy in various circumstances (biodegradable in soil and sea)
- ▶ PHAs can be processed (thermoplastic) with normal processing equipment like extrusion



Polyhydroxyalkanoates PHAs



Challenges with PHAs

- ▶ PHB has quite narrow processing window > Varying HV content can make processing easier
- ▶ Polyhydroxy alkananoates crystallize slowly > difficulties in some processes like film making because of sticky nature (before crystallizing)
- ▶ Post-crystallizing effect causes shrinking (dimensional changes)
- ▶ Nucleating agents can be used to speed up crystallizing > less or none post-crystallizing
- ▶ Brittleness in post-processing and in use
- ▶ Plasticizers and blends can be used to remedy brittleness
- ▶ Variation in quality between batches? > difficult to fixing/stabilizing of processing parameter between runs?
- ▶ Uneven quality of pellets? > uneven film? > pinholes?
- ▶ Linear polymer > high neck-in in cast film > thick edges > perhaps more waste



PHA grades and manufacturers

- ▶ Next slides present various manufacturers* producing PHAs
- ▶ Some are in development stage, some are commercially available in different scales
- ▶ Not all are suitable for film casting due to different purpose of use (for example injectin moulding)
- ▶ PHAs can be blended, plasticized and filled to gain more optimal properties in different uses → some companies specialized for this
- ▶ For example PHAs have been blended with PLA, PCL and PBS



PHAs grades and manufacturers 1 / 2

- ▶ **Danimer** (USA) > **Nodax®**, **formulated PHA** > "can be converted on existing equipment with minimal modifications" > <https://danimerscientific.com/pha-beginning-of-life/>
- ▶ **Biomer** (Germany) > **Biomer® PHB** > "can be processed with standard machine" > <https://www.biomer.de/IndexE.html> & haenggi@biomer.de
- ▶ **Natureplast** (France) > **NaturePlast PHA** > "primarily injection molding" > <https://natureplast.eu/en/matiere/phas-polyhydroxy-alcanoates/>
- ▶ **Kaneka** > **Kaneka PHBH™** > "different type of copolymer that can lead to different types of applications... custom create multiple grades of Kaneka PHBHTM ... a wide variety of traditional plastic shapes" > <https://kanekabiopolymers.com/>
- ▶ **Helian Polymers BV** (Netherlands) > **PHAradox** > "injection molding shown in web pages... custom made masterbatches can be developed" > <https://pharadox.com/>
 - ▶ Distributor of **Tianan Biologic** (China) **PHB**, **PHBV** (Enmat)

▶ **CONTINUED...**

PHAs grades and manufacturers 2/2

- ▶ **Ercros** (Spain) > **ErcrosBio PHA-based** > mainly injection moulding > http://www.ercros.es/index.php?option=com_content&view=article&id=1810:ercrosbio-pha-the-bioplastic-of-ercros-that-fights-against-marine-litter&catid=47&Itemid=800&lang=en
- ▶ **Gruppo Maip** (Italy) > **BIOS (PHB); lamNature® (PHB blend)** > film extrusion > <https://www.maipsrl.com/greenhope/biopolimeri?lang=en>
- ▶ **Navigate Corporation** (Czech) > **Hydal PHA, PHB** > "can be used for packaging materials... made of wastes" > <https://www.navigate.com/sustainable-packaging/>
- ▶ **Aimplas** (Spain) > **PHA formulation** > "Modification via the best route, physical or reactive extrusion: Bio and non-bio-additives" > <https://www.aimplas.net/processing-and-prototyping/compounding/bioplastic-developments/>
- ▶ **Tianjin Greenbio Materials** > **PHA, SoGreen™** > "PHA foam pellets" > <http://www.tjgreenbio.com/en/about.aspx>

PHA processing in BioBarr



PHAs from renewable sources



TAU conducts extrusion and casting into films



- ▶ Target was to extrude films for flexible packaging using PHA from renewable raw materials
- ▶ Processing of PHA has been done with existing machinery, i.e. with same extrusion machinery as traditional polymers are processed
- ▶ PHAs have typically very narrow processing window
- ▶ Crystallisation behaviour sets some challenges



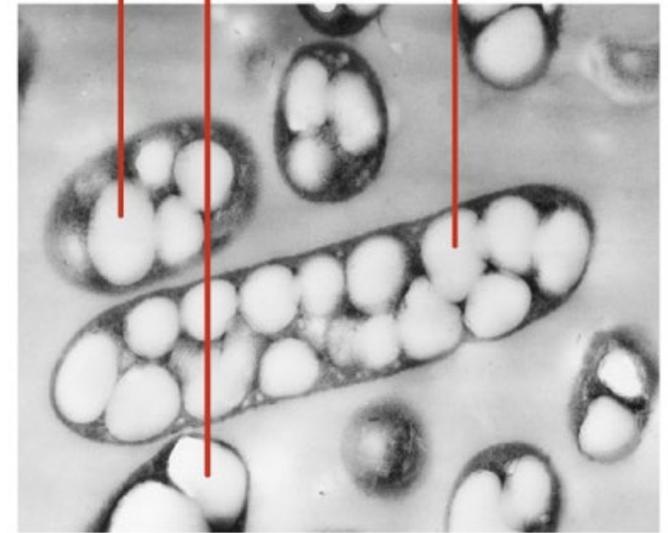
Treatments & lamination at ICI2 and package forming & packing at CORSINI
→ Bio-based packaging of bakery products



PHAs in BioBarr

- ▶ Different grades of PHAs studied in the project
 - ▶ **1st phase: MINERV™ from Bio-on (Italy)** <http://www.bio-on.it/>
 - ▶ Obtained from sugar co-products
 - ▶ PHBV
 - ▶ **2nd phase: 3 different commercially available PHA grades** were tested
- ▶ MINERV™ from Bio-on
 - ▶ MINERV "spheres" in white represent the MINERV-PHAs biopolymer obtained from sugar beets. These elements are the result of bacteria nourished by beet juices. Recovery is the next step in the process (recovery of PHAs) when Polyhydroxy alkanates are recovered and separated from the rest of the organic material of the cell. All waste materials (small amounts) are put back into the production cycle to feed new bacterial colonies along with the intermediate beet juice (exclusive Bio-on patent).
 - ▶ **Different formulations developed** (optimization of biopolymers trial by trial)
 - ▶ Fermentation > Recovery > Purification > PHA powder > Pellets for extrusion

Polyhydroxyalkanoates PHAs



MINERV™ from Bio-on - PHA formulation development

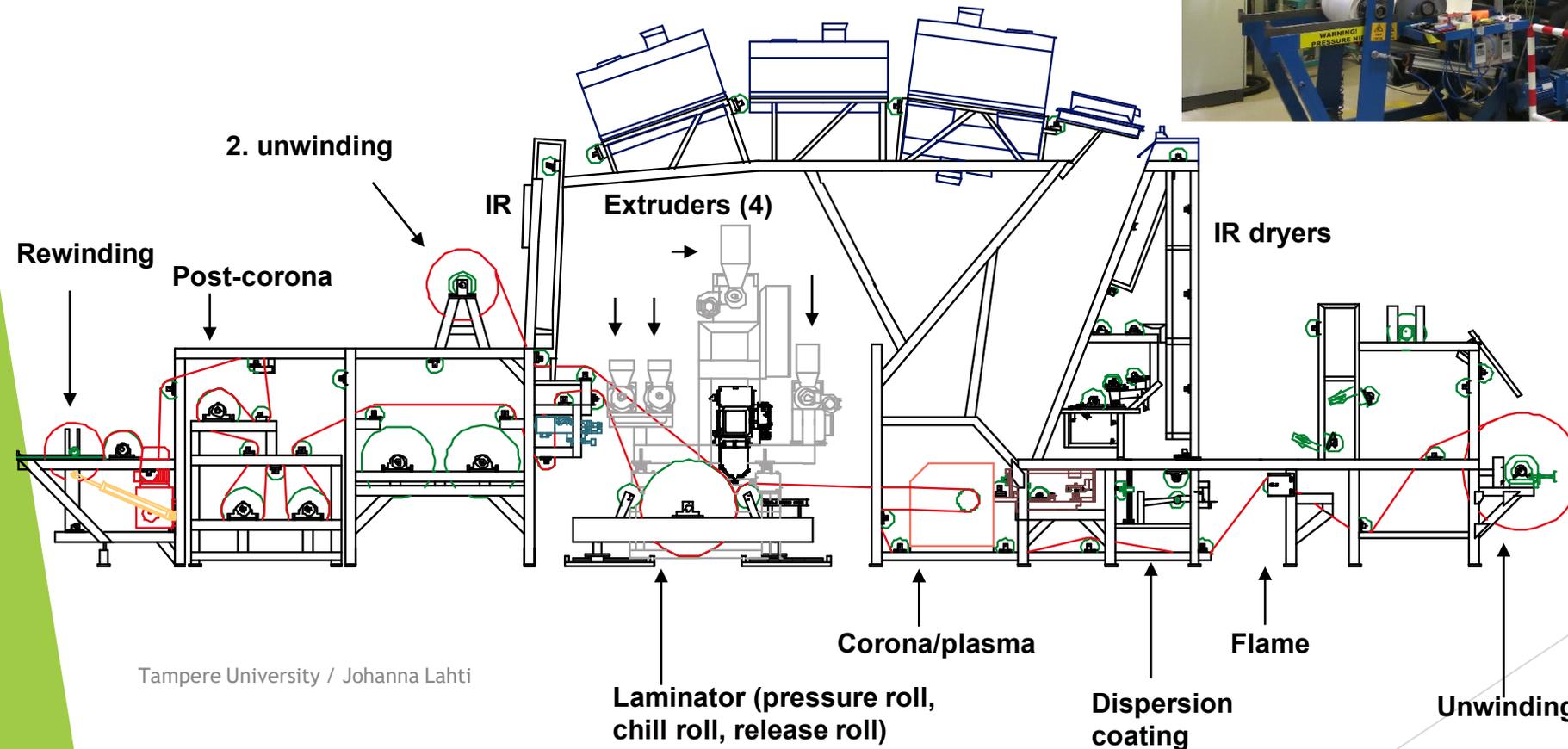
- ▶ **PHA recipe optimization:** e.g. molecular structure and additives taking into account the subsequent filming technology and the desired properties of the final film
- ▶ Formulations successfully tested in **blown film and cast film extrusion processes**
- ▶ Reduction of costs is possible, through:
 - ▶ optimisation of energy consumption in the last step of the recovery phase, the drying phase
 - ▶ reduction of chemical consumption in production process
 - ▶ use of wastes/co-products for producing biopolymers at competitive prices



(co)Extrusion coating/casting and lamination pilot line (TAU)



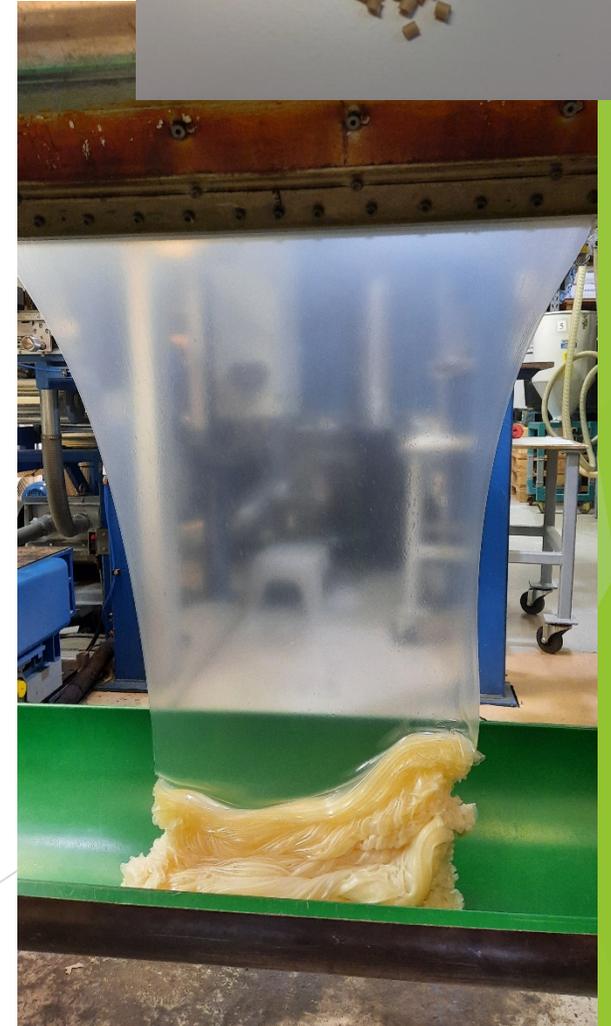
Air and air flotation dryers



- Coextrusion Coating
- Coextrusion Laminating
- Cast Film Coextrusion
- Surface Treatment
- Dispersion Coating
- Edge Trimming Service

PHA processing in BioBarr

- ▶ Different grades were tested:
 - ▶ PHA grades used in BioBarr: PHBV (Bio-on) and 3 commercial grades of PHB and PHBV
- ▶ Casted films produced in different thicknesses $< 80\mu\text{m}$
- ▶ Tested also in coextrusion with PLA and ecovio®
- ▶ Corona surface treatment tested for increasing surface energy
- ▶ Properties of films analysed: WVTR, OTR, grease barrier, heat sealability, mechanical properties, surface energy



Challenges overcome and to overcome

- + Processing of PHA has been done with existing machinery, i.e. with same extrusion machinery as traditional polymers are processed
- + PHAs have typically very narrow processing window → Suitable processing window found to produce uniform pinhole-free films
- + Crystallisation behaviour sets some challenges → Optimal casting set-up was found to avoid e.g. sticking problems
- Grade selection, i.e. really suitable for casting of films for flexible packaging
- Crystallisation behaviour → Mechanical properties and fragility in post-processing
- This project focused on "pure" PHA - in future studying of blending, coex and lamination



PHAs for packaging and other applications

- ▶ In BioBarr, PHAs have been demonstrated for
 - ✓ Blown film and cast film production → Films for flexible packaging
- ▶ In another TAU project PHA has been demonstrated also for extrusion coating of fiber-based substrate
- ▶ PHAs can be processed with existing extrusion equipment and are suitable for injection moulding and extrusion casting/coating methods for the production of coatings and objects.



Thank you for your attention!

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<https://www.tuni.fi/en/research/paper-converting-and-packaging>

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<https://www.biobarr.eu/>