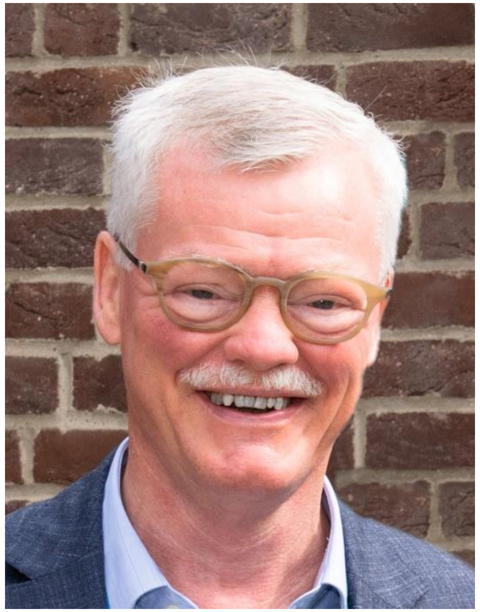
GO!PHA

Global Organization for PHA

Versatile End-of-Life options for AFTERLIFE products

9 October 2020

Introduction: Jan Ravenstijn



Experience:

- 22 years Dow Chemical
- 11 years DSM
- 27 years R&D
- 3 years Manufacturing
- 15 years global R&D director executive positions in engineering plastics, epoxies and elastomers' businesses
- 3 years USA, 4 years Germany, the rest in the Netherlands
- 3 years New Business Development → Biopolymers platform at DSM
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Current & recent activities since 2008

- Visiting professor Biopolymers at Eindhoven, Tsinghua and Dublin universities
- Consultant to international (EU, US, Asian, Japan) biopolymer companies and bio-refineries
- Consultant to investment and consulting companies, SMEs and OEMs
- Completed an extensive global bioplastics review paper (January 2010)
- Co-author of a bioplastics book for SMEs (Q1 2011)
- Member of the global expert team on renewable materials of the nova Institute
- Co-author of global market studies of the nova Institute (2013, 2015, 2017, 2018, 2019, 2020)
- Member Scientific Advisory Board Aachen-Maastricht Institute for Bio-Materials (AMIBM)
- Co-organizer of the PHA-platform World Congresses
- Co-founder and Board member of the Global Organization for the PHA-platform

TOPICS

1. What is PHA?
2. Status of the PHA-platform
3. Applications
4. End-of-Life in a circular economy
5. Closing remarks

1. What is PHA? (1)

- ✓ **PHA stands for Poly-Hydroxy-Alkanoate.**
- ✓ **Theoretically there can be an infinite number of PHAs.**
- ✓ **Claiming properties for or behaviour of PHA is a non-sense exercise. Even the well known PLA also belongs to the PHA class of materials.**
- ✓ **Specific PHA-polymers, like PHB and a number of its copolymers (like PHBV, PHBH, etc.) are not “plastics”, but are natural materials that are made and found in nature, like cellulose or starch.**
- ✓ **These natural macromolecular materials are not made by polymerization, but by enzymatically controlled biochemical conversion and they all have a role to play in nature.**

1. What is PHA? (2)

- ✓ **Of course not all natural materials biodegrade in every environment. Wood doesn't biodegrade in a marine environment, since the lignin in wood needs fungi to biodegrade and those are not present in sea water.**

- ✓ **PHB and its copolymers found in nature are part of the metabolism in all living organisms (plants, animals and humans) ever since there are living organisms on earth.**

- ✓ **Those specific PHA-materials function as nutritious and energy storage materials, so they are supposed to be used for that purpose. One can call that "biodegradation", but one could also call that "feed for living organisms in every environment".**

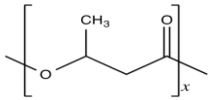
- ✓ **So the industrialization of the PHA-platform materials we talk about, consists of PHB and its copolymers PHBV, PHBH, PHBO, PHBD and P3HB4HB. The molecular structure of these are the same as what we find in nature.**

- ✓ **Details of these bio-benign materials, what they look like and how they perform will be covered in the next slides.**

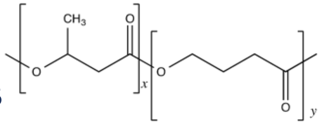
1. The industrial PHA product platform is very diverse…

- ✓ scl-PHAs → P3HB, P4HB, PHBV, P3HB4HB, PHB3HV4HV.

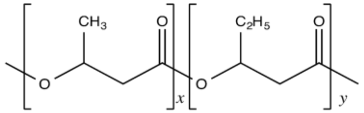
P3HB



P3HB4HB

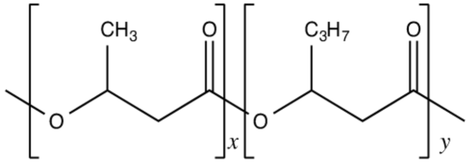


PHBV

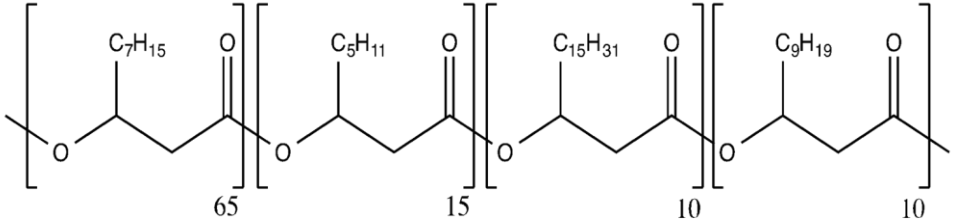


- ✓ mcl-PHAs → PHBH, PHBO, PHBD.

PHBH



- ✓ lcl-PHAs → Many varieties possible.



scl:	short chain length
mcl:	medium chain length
lcl:	long chain length

In addition PHAs have been designed with aromatic or C=C groups in the side chain.

1. … so the properties vary quite a bit

Properties of PHA-platform materials										
Polymer	PHB	P3HB4HB Tianjin Green Biomaterials			PHBV Phario			PHBHx Kaneka		PHA-platform
		10% 4HB	20% 4HB	40% 4HB	20% HV	30% HV	40% HV	6% HHx	11% HHx	
Mw kD		970	810	530						300-1,000
Tmelt °C	175	127	104	59	150	125	97	145	126	60-175
Tg °C		0	-10	-21	-1	-3	-4	2	0	≤0
Tensile Modulus MPa	>3,000	955	225	4				1,820	950	<10 - >3,000
Tensile Yield MPa	45	20	8	0.4	24	20	12	36	26	<1 - 45
% Elongation	<1	180	680	1,350	20	35	>250	4	320	<1 - >1,000

→ **Chemically produced PHBV (20%) has TY of 15 and 350% E**

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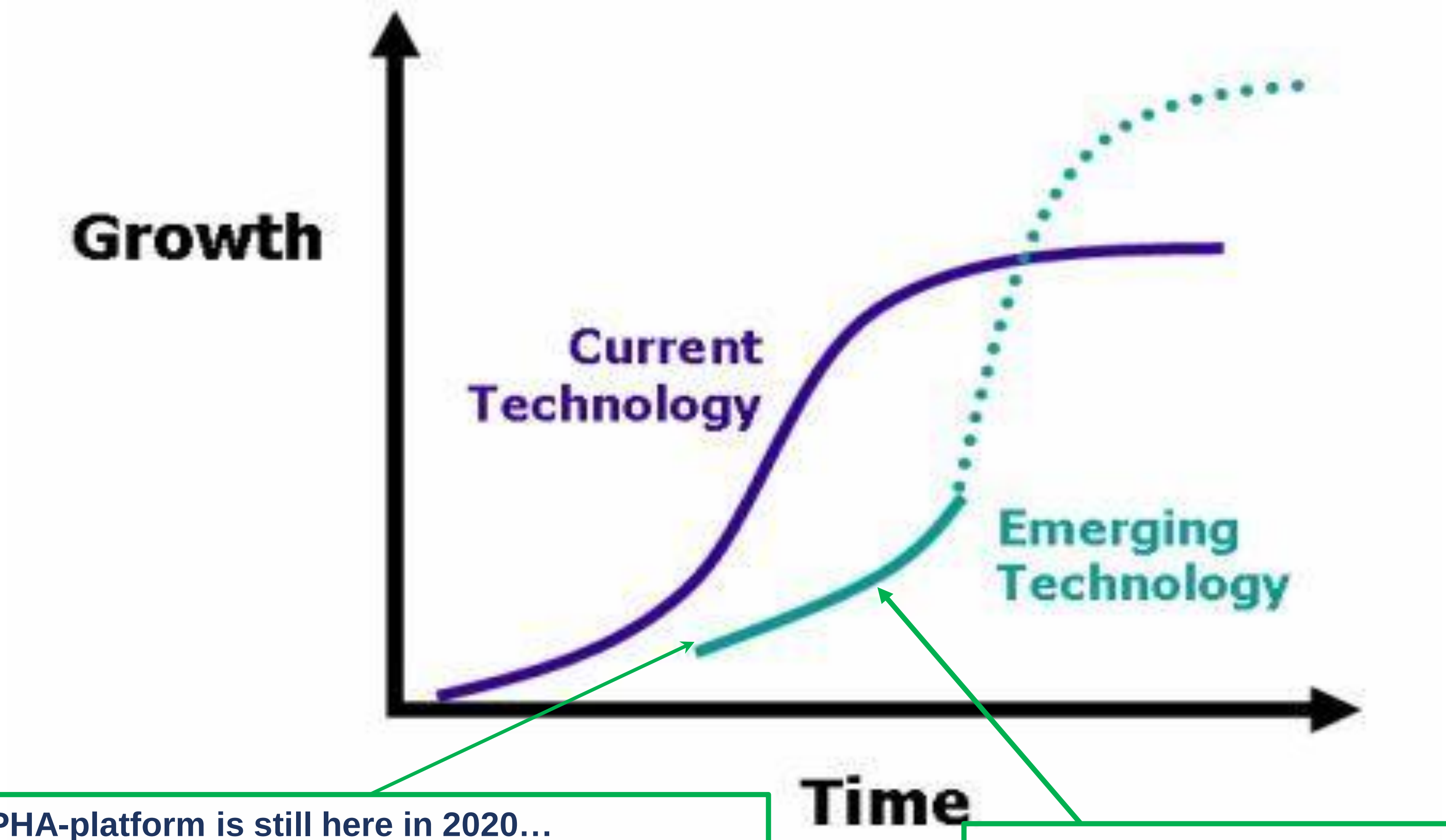
2. PHA-platform on the S-curve



PHA-platform is still here in 2020…

…but is expected to move to the next stage soon.

2. Many Renewable Carbon sources for PHA-polymers

- In 2006 Metabolix announced construction of the first large scale PHA plant based on corn: 50 kt/annum.
- 12 years ago the main feedstock sources were corn, sugar and vegetable oils.
- Today many PHA start-ups and SMEs are working on using flue gases, waste water streams, plastic waste, waste cooking oil and other waste streams (like from sugar, fruit & palm oil industries) as feedstock →
  → Carbon from the biosphere, atmosphere and technosphere.
- Most commercial PHA manufacturers also pursue the use of 2nd generation feedstock to lower the costs and to counsel issues over "competition with the food chain".
- They also see this as a more valuable option than using those streams for energy.

2. Bacterial strains ←→ Feedstock & co-nutrients

- ✓ **There are many different bacterial strains, both unmodified and gene-modified, that can and do make a large variety of PHA-polymers.**
- ✓ **Wild type bacterial strains can be and are turned into producers of multiple PHA-polymers and –copolymers which depends on the use of co-nutrients.**
- ✓ **Metabolic engineering of bacterial strains for production of PHA-polymers is a must nowadays to ensure process competitiveness, both from a cost as well as from a product quality and quality consistency perspective.**
- ✓ **Metabolic engineering also creates a new biochemical pathway for co-nutrient supply based on renewable feedstock, but they still generate PHA-polymers that also appear in nature.**

2. PHA challenges & status

Remaining challenges of the current commercial PHAs are:

- **Molecular chain scission above 160 °C → control processing operating window**

  Lowering T_m, low-shear screw designs, building in 4HA and/or 2HA moieties all help to open up the processing window.

- **Slow nucleation from the melt → long process cycles**

  Several effective nucleating agents have been found/developed, but this is not common knowledge yet.

- **Legislation → Threat or opportunity?**
- **Expensive!? → Starting industry at the beginning of the S-curve.**
- **Availability? → Demand exceeds supply by far in 2020.**

2. Some PHA players today – October 2020

Company	Feedstock	Strain	Product	Capacity in place	Capacity planned
PHB:					
Nafigate	Waste oil - palm oil	Unmodified	PHB	Pilot	First plant in 1st half 2021
Tianan Biologic Material	Corn starch glucose	Unmodified	PHB & PHBV (2%)	2 kt/annum	Expands to 10 kt/annum
P3HB4HB:					
Bluepha	Organic waste streams	Modified	P3HB4HB (15%)	1 kt/annum	?
CheilJedang	?		P3HB4HB (50%)	Pilot	Plans next scale
PHABuilder*	?	Halomonas modified	P3HB4HB (several)	1 kt/annum	Starts 3 units of 1 kt/annum
PHBV:					
Bio-On	Glycerol, starch, sugars	?	PHB & PHBV	1 kt/annum	Company gets new owner
Full Cycle Bioplastics	Pre-consumer food waste, green bin	?	PHBV (several)	Pilot	Prepares for next scale step
Newlight Technologies	Biogas, CO2	?	PHB & PHBV (?)	5 kt/annum?	Just started a new line.
Phario	Fatty acids from waste water	Unmodified	PHBV (several)	Lab scale	Announced Pilot plant for 2021
PHBH:					
Danimer Scientific	Canola oil	Modified	PHBH (several)	2 + 8 kt/annum	+12 kt/annum in 2021
Kaneka	Palm oil, waste streams	Modified	PHBH (several)	5 kt/annum	+20 kt/annum in few years
PHABuilder*	?	Halomonas modified	PHBH (several)	1 kt/annum	Starts 3 units of 1 kt/annum
RWDC-Industries	Waste cooking oil	Modified	PHBH (several)	5 kt/annum	+25 kt/annum in 2021

3. Applications … understand USPs for the whole value chain

Most mechanical, rheological, thermal and optical property combinations offered by the new bio-based polymers are also offered by the traditional fossil-based polymers.

→ Those properties are Qualifiers, no Differentiators

However, in some cases we see some attractive new performance characteristics, like:
→ PEF for bottles shows significantly better barrier properties than PET;
→ PLA for fibers shows excellent wicking and high colour intensity upon dyeing;
→ PHA …… what about it? → haptics / soft touch / versatile biodegradability / mimicking nature;

3. PHA unique selling points

Although the PHA product family consists of a broad range of products, a combination of the following USPs can be applicable for different applications:

- ✓ **Boosts brand image**
  - GHG-emission
  - No competition with food chain (Wave II or GHG feedstock)
  - No GMO in feedstock
- ✓ **Very versatile biodegradability characteristics**
  - Aerobic Industrial & Home composting
  - Marine & Soil degradability
  - Anaerobic digestion
- ✓ **Compatibility - Behaviour**
  - Unique haptic properties combined with matting effect
  - No coupling agents or other expensive additives required in blends or composites
  - Excellent physico-chemical properties (printing, sealing, dyeing, barrier)
  - Forms a one-phase system with PVC as flow promotor, reinforcement of PLA
  - What about the compounds in combination with Cellulose esters or APCs?
- ✓ **Bioresorbable**
  - Watch purity
  - P3HB and P4HB

3. Applications / market segments for PHA

- PHA-products range from amorphous to highly crystalline, from “high strength, hard and brittle” to “low strength, soft and elastic”:
  - → Quite different application areas for specific types of PHA!
  - → Which PHA-polymer do or can you make?

- PHA-products cannot fully substitute any of the existent fossil-based polymers, but they can partly replace most of them:
  - → The accessible market for PHA is hundreds of kilotonnes/annum if the cost/performance-balance is OK.

- Application areas:

  Injection moulding, sheet and film extrusion, thermoforming, foam, non-wovens, fibers, 3D-printing, paper coating, glues, binders, adhesives, additives (reinforcement, plasticization), UPR and PUR building block.

3. PHA applications …… demonstrated high versatility

Possible Product Market Combinations:

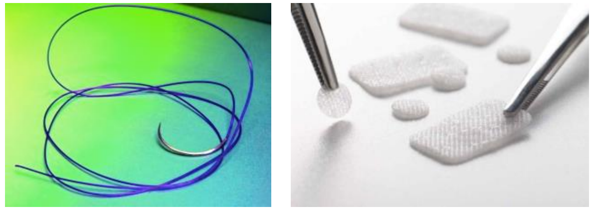
1. Feed
2. Films
3. Fibers
4. Foams
5. Furniture
6. Stationary
7. Cosmetics
8. Appliances
9. Sunscreens
10. Fishing gear
11. Chewing gum
12. Cheese coating
13. Synthetic paper
14. Animal nutrition
15. Fertilizer coating
16. Electrical switches
17. Paints and Coatings
18. Biomedical Materials
19. Cosmetic applications
20. Thermoplastic Elastomers
21. Waste-water & aquaria denitrification
22. Glues & Adhesives i.e. pressure sensitive adhesives
23. Engineering Plastics for automotive, electronics, etc.
24. Microparticles (abrasives, sunscreens, exfoliants, etc.)

One type PHA-product cannot do everything though.

Most of these applications have been demonstrated already.

3. Demonstrated PHA applications (commercial)

Spectacle case
e.g. MAIP (PHBH)



Medical and surgical applications
e.g. Tepha (P4HB)

Flexible packaging
e.g. PHBV

Sewage treatment
e.g. Tianan, Helian Polymers

Organic waste bags
e.g. Ecomann (P3HB4HB)

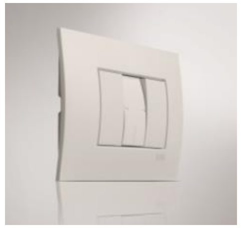
Stationary
e.g. MAIP (PHBH)

Food tray
e.g. FKuR

Exfoliating microbeads (scrub)
e.g. Orkla, Nafigate (PHB)

Organic Chair
e.g. Kartell – Sabio

Plant clip
e.g. Metabolix



Durable E&E light switch
e.g. ABB, MAIP, Kaneka partnership (PHBH)

Sea current tracking buoys
e.g. Metabolix (P3HB4HB)

Flexible packaging
e.g. PepsiCo – Danimer pre-commercial partnership (mcl-PHA)

4. Natural PHA-products fit very well with a circular economy

- ✓ **PHB and a large number of its copolymers are made and used in nature all the time:**
  1. **They are made by bacteria from available nutrients and by enzymatic synthesis;**
  2. **They are used as nutrients and energy providers by living organisms resulting in CO_2, water and biomass/compost;**

- ✓ **This circular system is much older than mankind.**

- ✓ **By using these materials for construction applications (films, parts or even glues) that circular behaviour can both be used and be extended.**

- ✓ **An additional advantage of these specific PHA materials is that they can fully meet a comprehensive combination of end-of-life options fitting a circular economy, very much like cellulose or starch.**

- ✓ **Before using them in an application one should carefully consider the “Reduce” and “Re-design” principles.**

4. End-of-Life options for natural PHA-products (1)

Polymeric materials that can fully meet a comprehensive combination of End-of-Life options include cellulose, a large number of PHA-polymers and starch, or a combination of each of these:

1. **Recycle articles to be used again:**
   → Can be done many times, but be aware of micro-plastic generation (textiles)

2. **Recycle articles back to the polymer:**
   → Can be done 2 or 3 times, so it's not a holy grail for any polymer!!!

3. **Recycle articles back to raw materials:**
   → Generates Renewable Carbon which can be used for many products

4. End-of-Life options for natural PHA-products (2)

4. Recycle articles to environment (home, industrial) composting:
   → Useful for articles that inevitably end up contaminated with organic waste

5. Recycle articles to energy (incineration):
   → Useful for bio-energy generation, but don't forget to use the CO_2 as feedstock

6. Recycle to nutrients for living organisms:
   → All living organisms feed on nutritious materials. In addition several PHAs take care of denitrification (waste water streams, aquaria, fish ponds).

Many fossil-based polymers do not meet all these End-of-Life options, while they all should be required to meet them if they, intended or by accident, can end up in the environment.

All these End-of-Life options contribute to a Circular Economy.

One simply cannot avoid the necessity for any of the End-of-Life options mentioned.

4. Not all natural materials are biodegradable in all environments …

- **Starting point should be: "Materials allowed for Single Use applications should not be harmful to the environment in any way when they purposely or accidentally end up in the environment". They also need to biodegrade in a marine environment.**

- **Cellulose (paper), Starch and P3HB and its copolymers fit that description.**

- **Wood is not biodegradable in a marine environment, since lignin (50% of wood) needs fungi for biodegradation while they are not present in the marine environment.**

Biodegradable Polymers in Various Environments

NOTES

proven biodegradability

proven biodegradability under certain conditions or for certain grades

biodegradability not proven

The biodegradability of plastics derived from these biodegradable polymers can only be guaranteed if all additives and (organic) fillers are biodegradable, too. Dying and finishing of cellulosic fibres, for example, may prevent their biodegradation in the environment.

Biodegradability depends on the complex biogeochemical conditions at each testing site (e.g. temperature, available nutrients and oxygen, microbial activity, etc.). Therefore, these generalised claims about biodegradation can only serve as approximations and need to be confirmed by standardised testing under lab conditions. In-situ behaviour can vary, depending on the mentioned conditions, size of the plastic, grade of the polymer and other factors. For instance, biodegradation testing is often performed after milling, showing the inherent nature of the material to biodegrade. In reality, the same level of biodegradation will be obtained, be it possibly within a different timeframe.

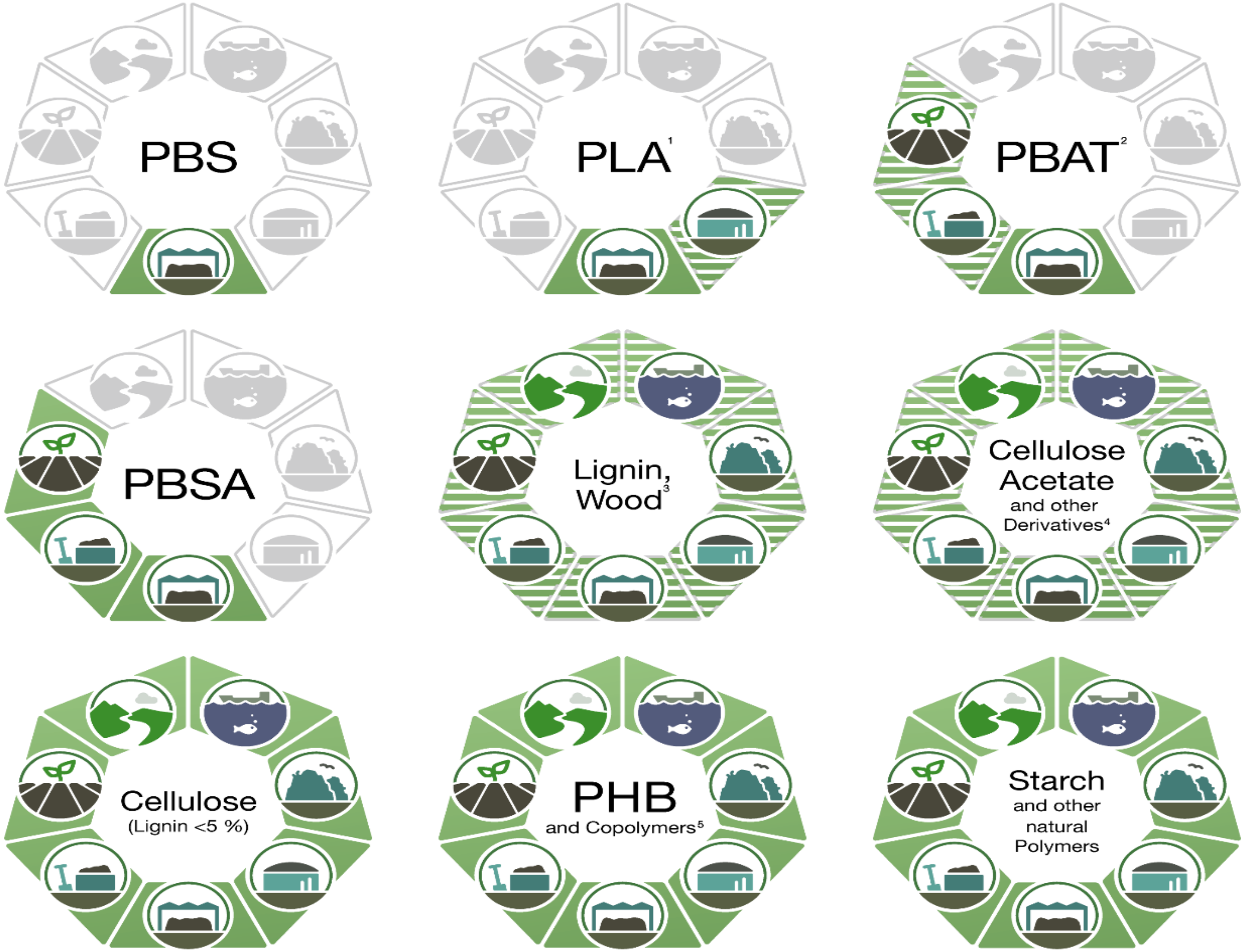
1 PLA is only likely to be biodegradable in thermophilic anaerobic digestion at temperatures of 52°C.

2 Biodegradability in home composting and in soil of PBAT is only proven for certain polymer grades.

3 Complete biodegradation of materials with a high lignin content is not easily measurable with standard biodegradation tests, but does take place (slowly). Instead of CO_2, especially humus is produced by the biodegradation of lignin-rich materials.

4 The biodegradation of CA in all environments is only proven for certain polymer grades.

5 incl. P3HB, P4HB, P3HB4HB, P3HB3HV, P3HB3HV4HV, P3HB3Hx, P3HB3HO, P3HB3HD



ENVIRONMENTS

Details on test conditions and, if available, applicable pass/fail criteria.

MARINE ENVIRONMENT
Temperature 30°C, 90% biodegradation within a maximum of 6 months (Certification: TÜV AUSTRIA OK biodegradable MARINE (ISO under preparation))

FRESH WATER
Temperature 21°C, 90% biodegradation within a maximum of 56 days (Certification: TÜV AUSTRIA OK biodegradable WATER)

SOIL
Temperature 25°C, 90% biodegradation within a maximum of 2 years (Certification: TÜV AUSTRIA OK biodegradable SOIL; DIN Certco DIN-Geprüft biodegradable in soil)

HOME COMPOSTING
Temperature 28°C, 90% biodegradation within a maximum of 12 months (Certification: TÜV AUSTRIA OK compost HOME; DIN Certco DIN-Geprüft Home Compostable)

LANDFILL
No standard specifications or certification scheme available, since this is not a preferred end-of-life option

ANAEROBIC DIGESTION
Termophilic 52°C / mesophilic 37°C; standard specification not yet available, but 90% generally considered as completely biodegradable

INDUSTRIAL COMPOSTING
Temperature 58°C, 90% biodegradation within a maximum of 6 months (Standard: EN 13432)

www.bio-based.eu

More figures available at www.bio-based.eu/graphics

Partners: IKT Kunststofftechnik Stuttgart; OWS; Hydra Marine Sciences

Sponsors: TÜVRheinland DIN CERTCO; TÜV Austria

Your feedback is welcome: michael.carus@nova-institut.de

4. Biodegradation in deep-sea

Looking at the deep sea situation with temperatures ranging between 10 and 4 ºC we expect the following based on tests and estimations:

Material	Years to 90% degradation	Comments
Cellulose	0.5 to 1	Faster at higher T
PHBV (17%)	4 to 7	Same order of magnitude
Wood	500 to 1,000 ?	Shipwrecks 500+ years
PP, PLA, PET	"Never"	Don't use for SUPs

Cellulose and PHBV studied at MSU.

5. Closing remarks

- ✓ The PHA-platform is the first polymer family produced by fermentation and is moving from the embryonic stage to the early-growth stage.
- ✓ Different PHA product families can be used for a broad range of applications → construction, adhesives, additives, thermosets.
- ✓ New volumes built and started up and there is more to come.
- ✓ The mcl-PHAs currently make the main move, but scl-PHAs seem to be right behind them.
- ✓ Several of the old challenges (nucleation, process-ability) have been taken care of.
- ✓ For PHB and its copolymers all known End-of-Life options are possible and all lead to a circular economy.
- ✓ Main challenges now are availability and upcoming legislation.