ARC Training Centre for Bioplastics and Biocomposites

The University of Queensland Australia

How Fillers and Functional Additives Impact the Biodegradation of Polyhydroxyalkanaote (PHA)?

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38APS

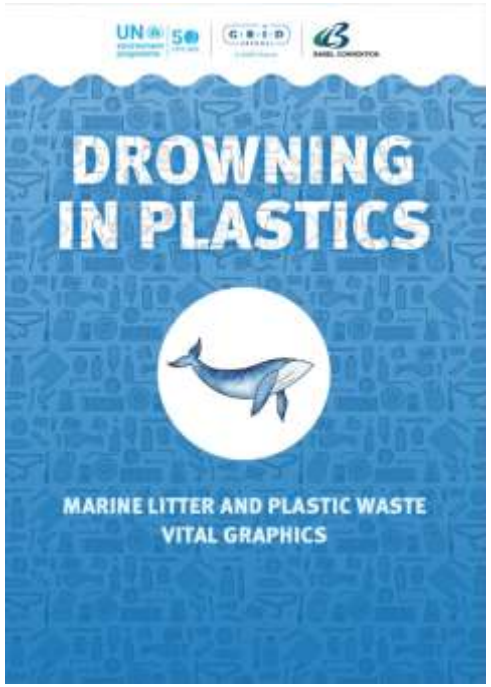
Plastics are Now Ubiquitous in Our Lives

Figure from Lackner, M., *Biopolymers*, in *Handbook of climate change mitigation and adaptation*, W.-Y. Chen, T. Suzuki, and M. Lackner, Editors. 2017, Springer International Publishing: Switzerland. p. 3211-3230.

Shift Towards Biodegradable Plastics

Plastic waste has been described as one of the most pressing environmental issues of our time

- Most plastics are produced from fossil fuels
- Each year, ~20 Mt of plastic waste leaked into the environment
- Australia has a very low plastics recycling rate



Biodegradable plastics present a potential solution, but their role in an increasingly circular economy is not straight forward.

Bioplastics Are not Just Biopolymer!

- Plastic additives and fillers are added to ‘make biopolymer better’

Functional additives
(e.g. plasticiser, stabiliser, flame retardant, antioxidant)

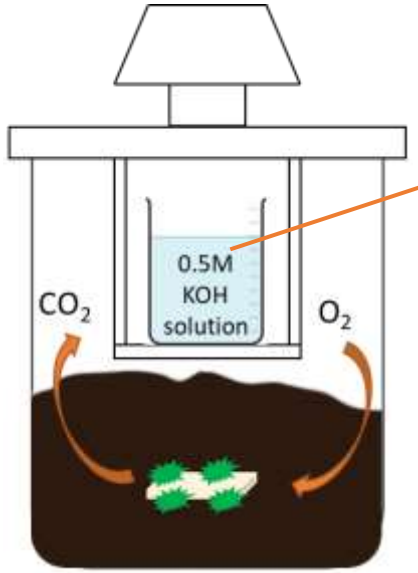
Colourants & Dyes

Fillers & Reinforcement

How? Biodegradation Assessments

- Field trial in natural (inactive) soil at a fully monitored field trial site in sub-tropical Queensland (27.5° S, 152.9° E)
  - Mass Loss; Physical properties; Mechanical properties

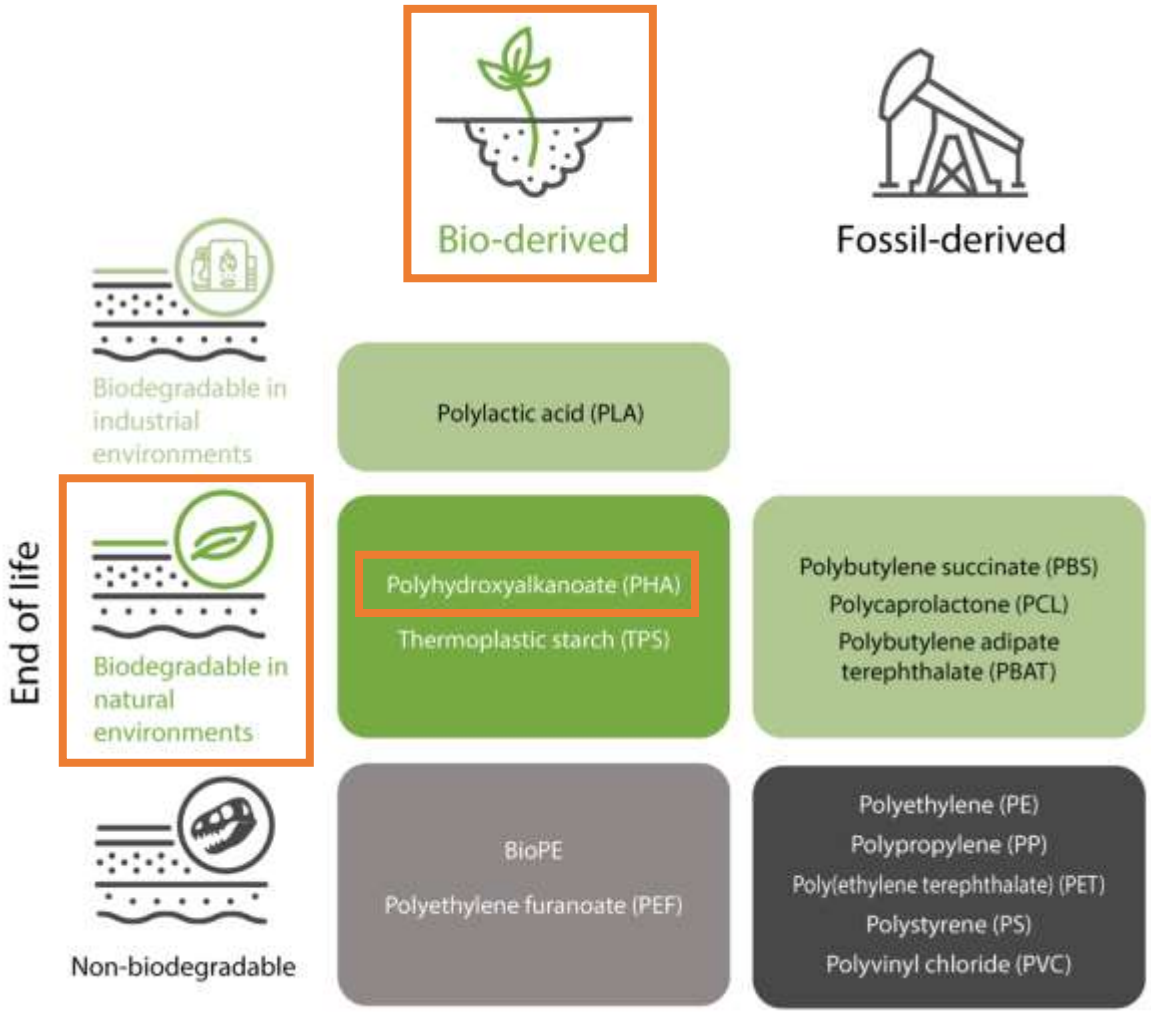
- Lab-based test complying with current soil biodegradation testing standards (ISO 17556) using OxiTop systems
  - CO_2 evolution / O_2 consumption



CO_2 emitted trapped in KOH solution

Negative pressure generated from consumption of O_2 from microbial activities

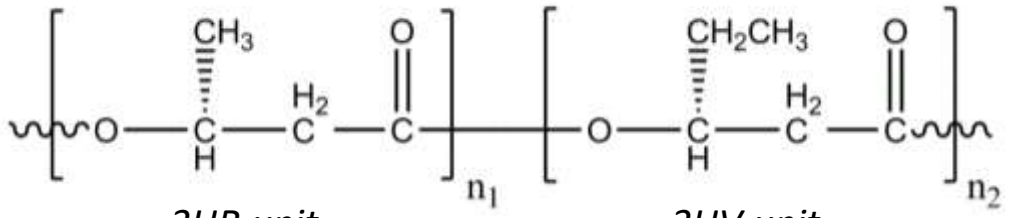
Our Model Bioplastic: Polyhydroxyalkanoate (PHA)



Our model bioplastic:

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV):

- Displays all the features characterising 'green' plastics
- 1 mol% 3HV content
- $\overline{M_n}$ = 192 kDa, $\overline{M_w}$ = 455 kDa, PDI = 2.3



3HB unit *3HV unit*

Effect of an Abundant Natural Fibre

Representative Natural filler/fibre:

Radiata Pine wood flour

- Abundant natural fibre
- Take advantage of wood being low-cost and with reinforcing effects
- Final biocomposite product is still bio-derived and biodegradable

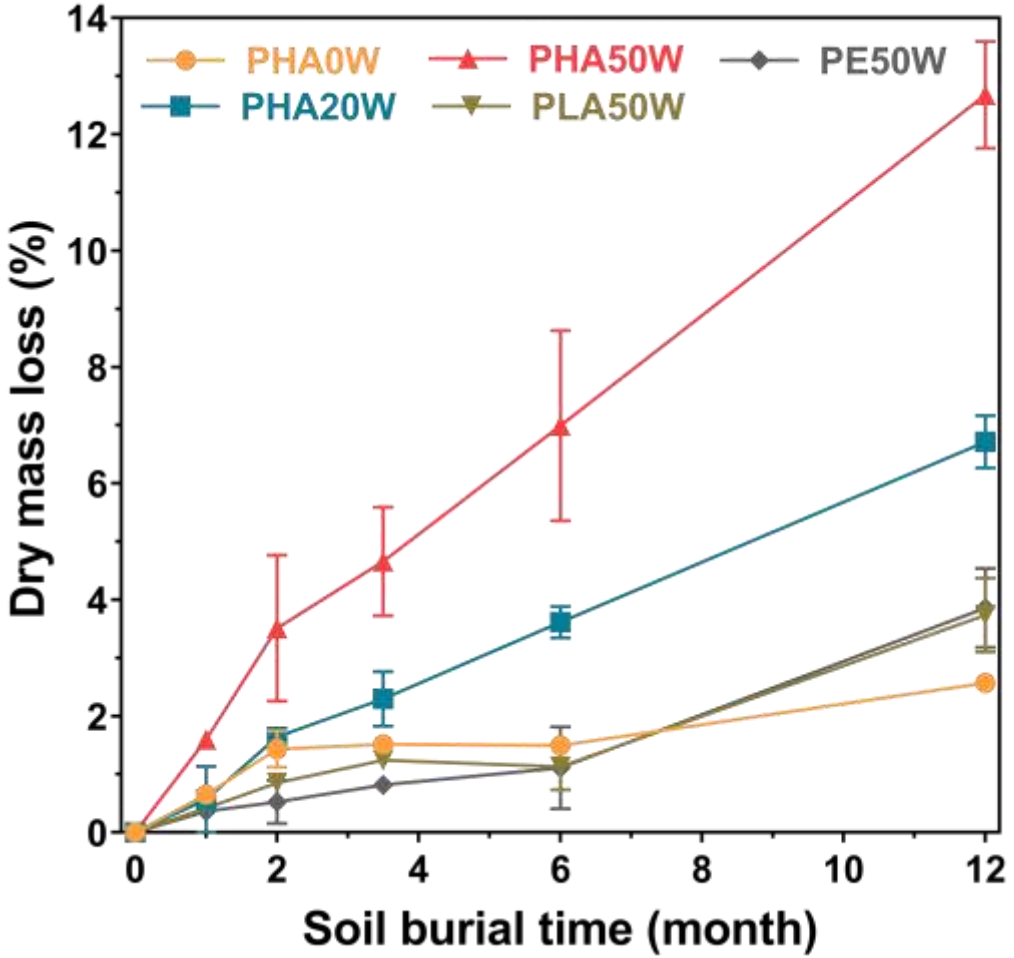
Medium:	Natural soil	
System:	Mass loss from field trial	CO_2 evolution using OxiTop
Duration:	12 months	54 months

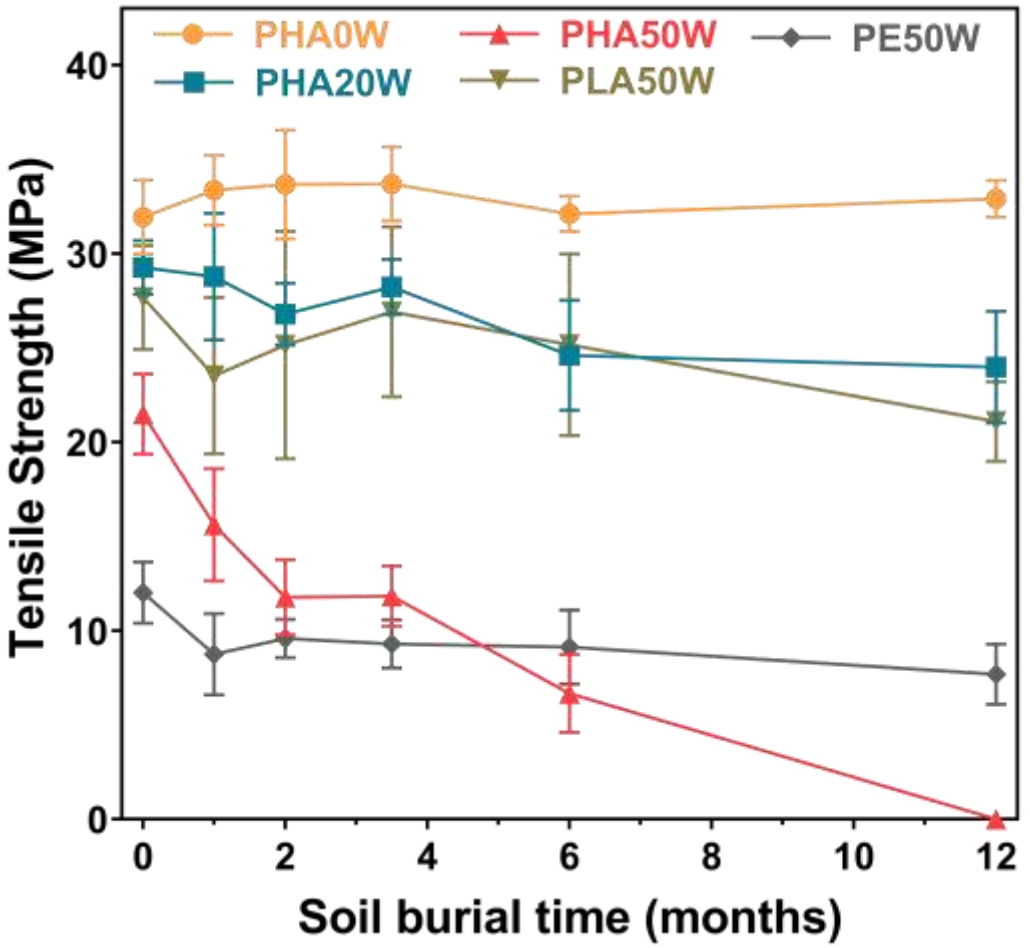
Samples:
(70 x 15 x 1.5 mm) compression moulded strips (~2.5 g)

In 10 replicates:

1. PHBV (PHA0W)
2. PHBV with 20 wt% WF (PHA20W)
3. PHBV with 50 wt% WF (PHA50W)
4. PLA with 50 wt% WF (PLA50W)
5. PE with 50 wt% WF (PE 50W)

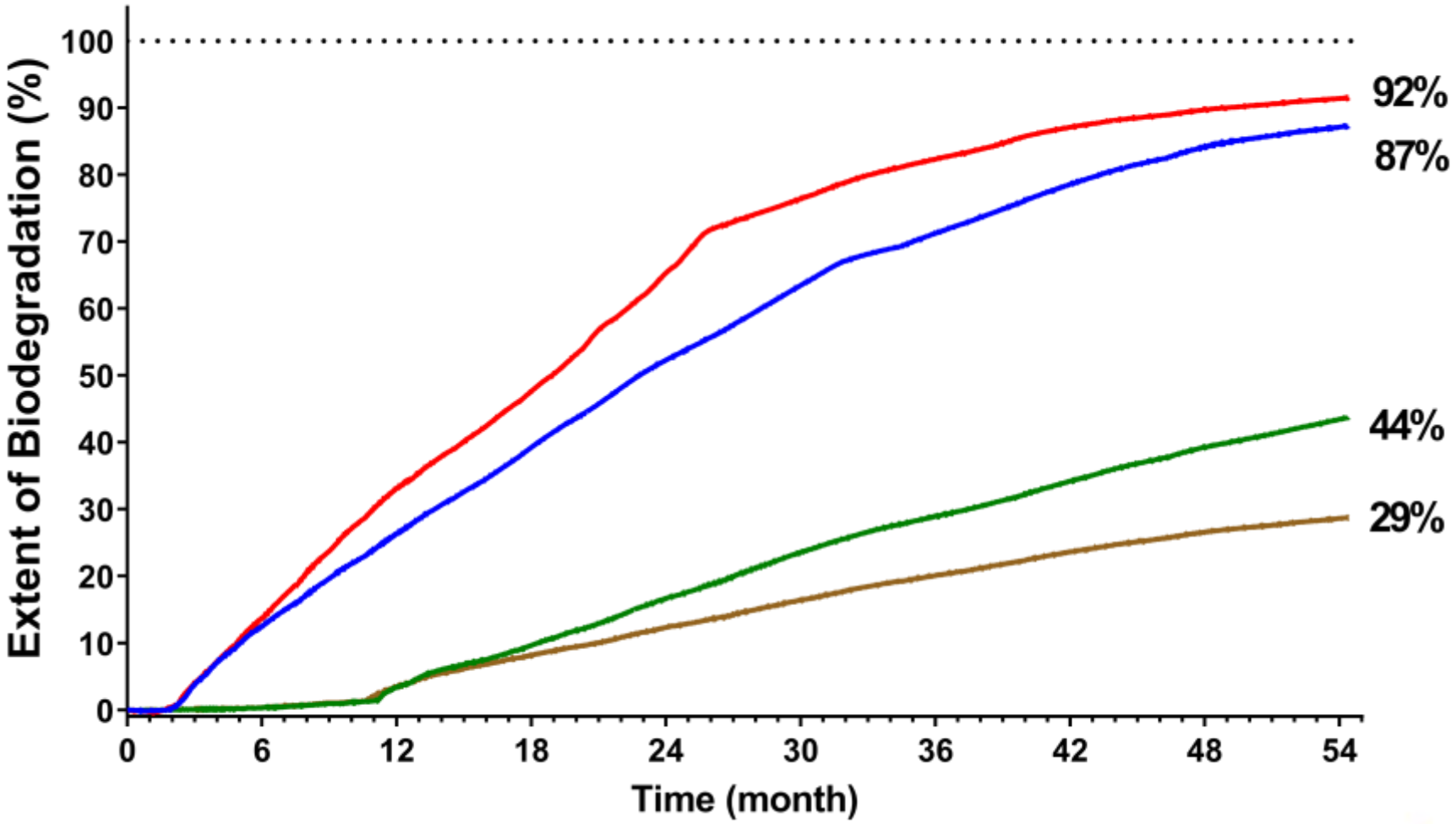
Lifetime (Mass) VS Performance Lifetime





Chan, C.M., et al., *Insights into the biodegradation of PHA / wood composites: Micro- and macroscopic changes.* Sustainable Materials and Technology, 2019, 21, e00099

Biodegradation Curves – CO_2 Evolution



Lag-time:

PHA20W = PHA50W

PLA50W = PE50W

Biodegradation rate:

PHA50W

PHA20W

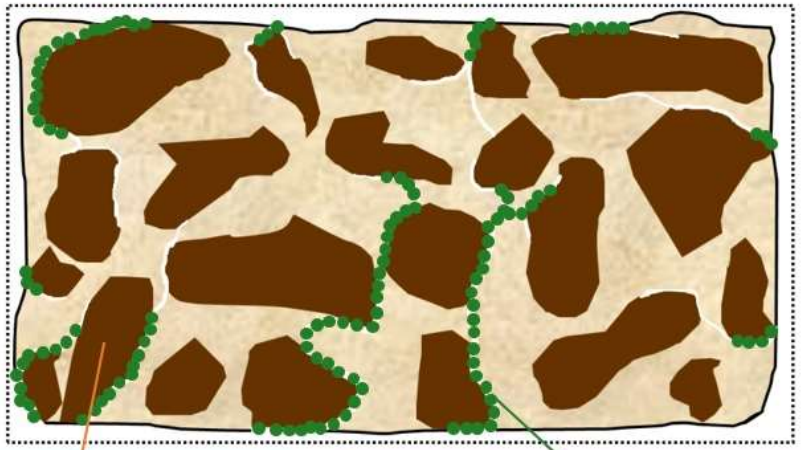
PLA50W

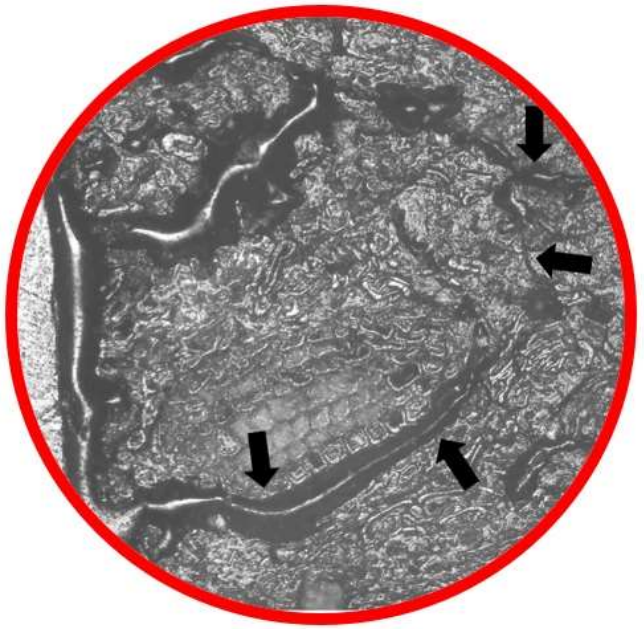
PE50W

Unpublished data

Mechanism – Effect of Natural Fibre

- PHAs show surface erosion mechanism
- Formation of cracks and channels
- Penetration of microorganisms, or at least relevant enzymes, into the bulk to catalyse degradation





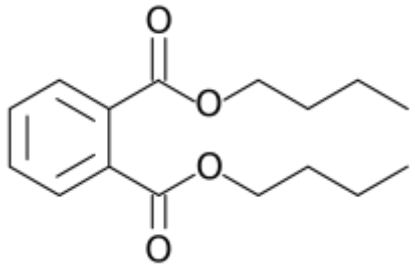
Formation of cracks along the interfaces

Effect of a Traditionally Used Plasticiser

Representative plastic additive:

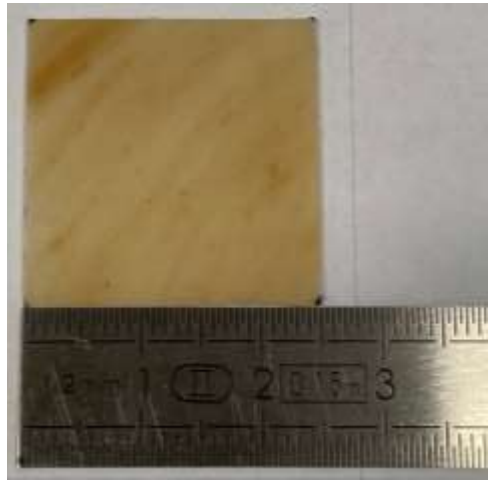
Dibutyl phthalate (DBP)

- Widely-used as plasticiser (10-70% loading) for plastics in processing
- Known ecotoxicity
- Banned in several countries, used here only as a model compound



Medium:	**Standard soil (ISO 17556)**
System:	CO_2 evolution using OxiTop
Duration:	18 months

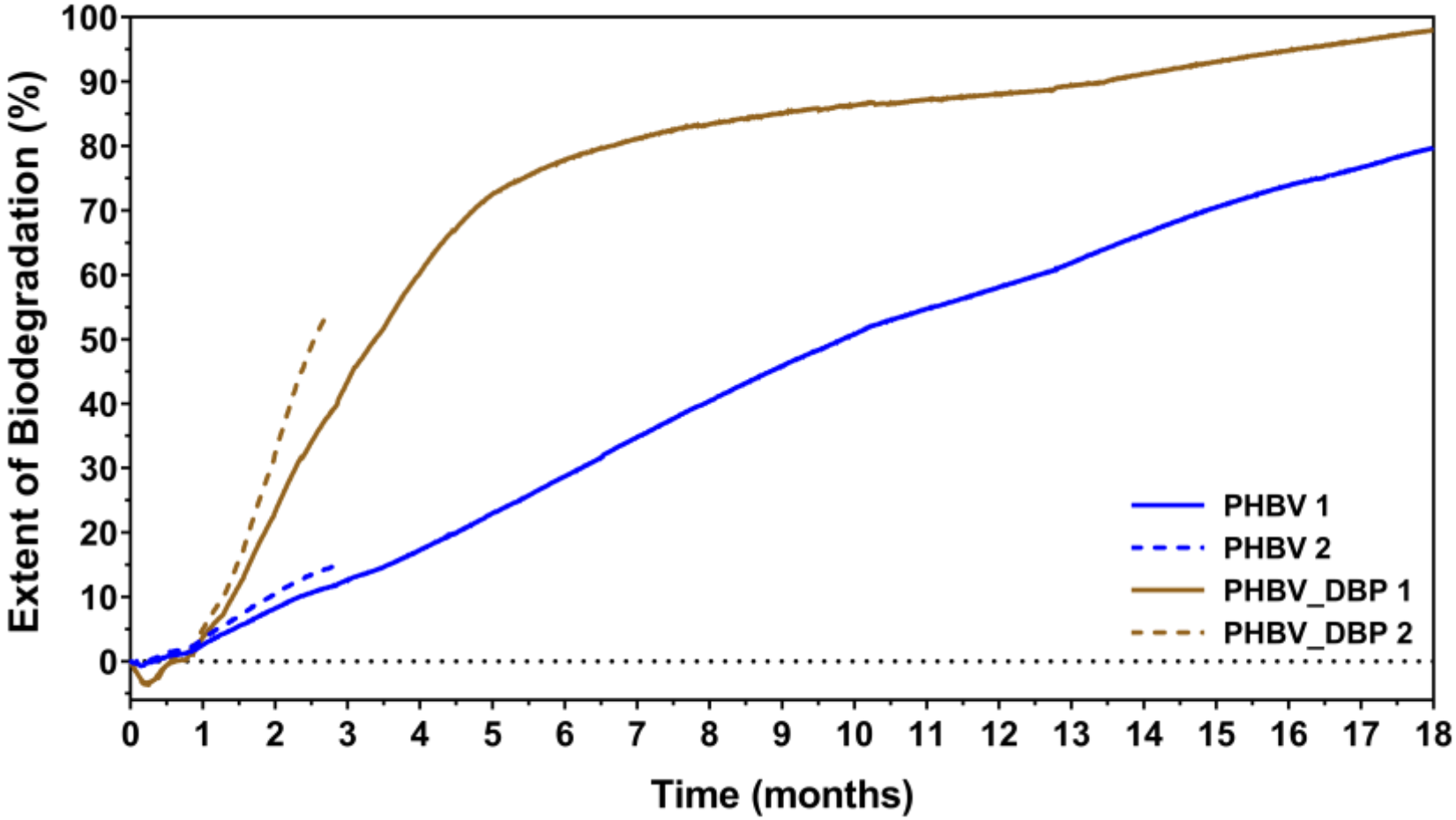
Samples:
(25 x 25 x 1 mm) compression moulded sheets (~0.8 g)



In duplicates:

1. Neat PHBV (PHA)
2. PHBV with 20 wt% DBP (PHA_DBP)
3. Soil only (negative control)
4. Starch powder (positive control)

Biodegradation Curves – CO_2 Evolution



Lag-time:

PHBV with DBP

❯

Neat PHBV

Biodegradation rate:

PHBV with DBP

❯

Neat PHBV

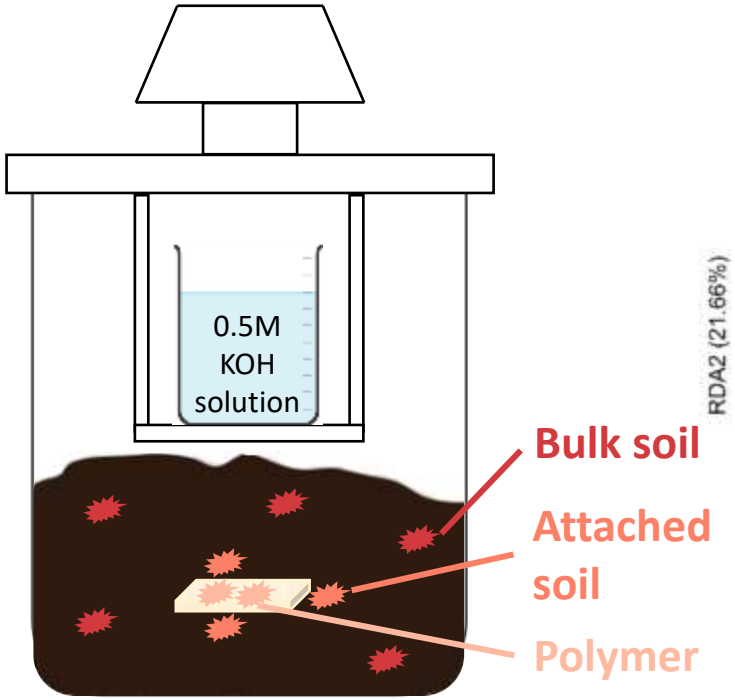
PHBV

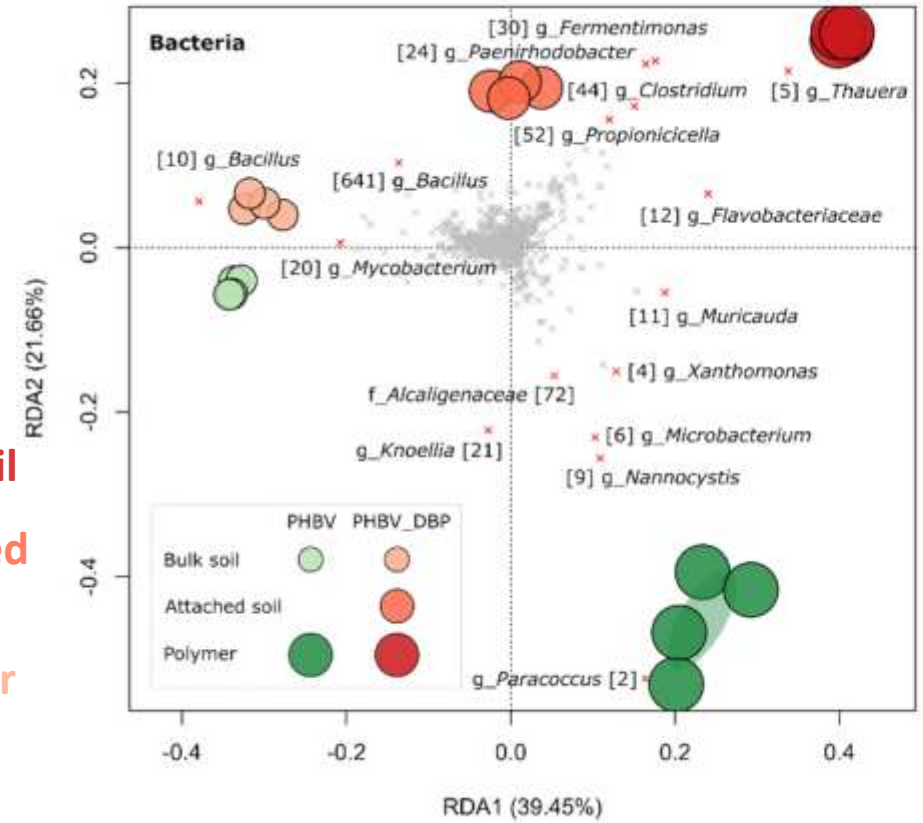
PHBV_DBP

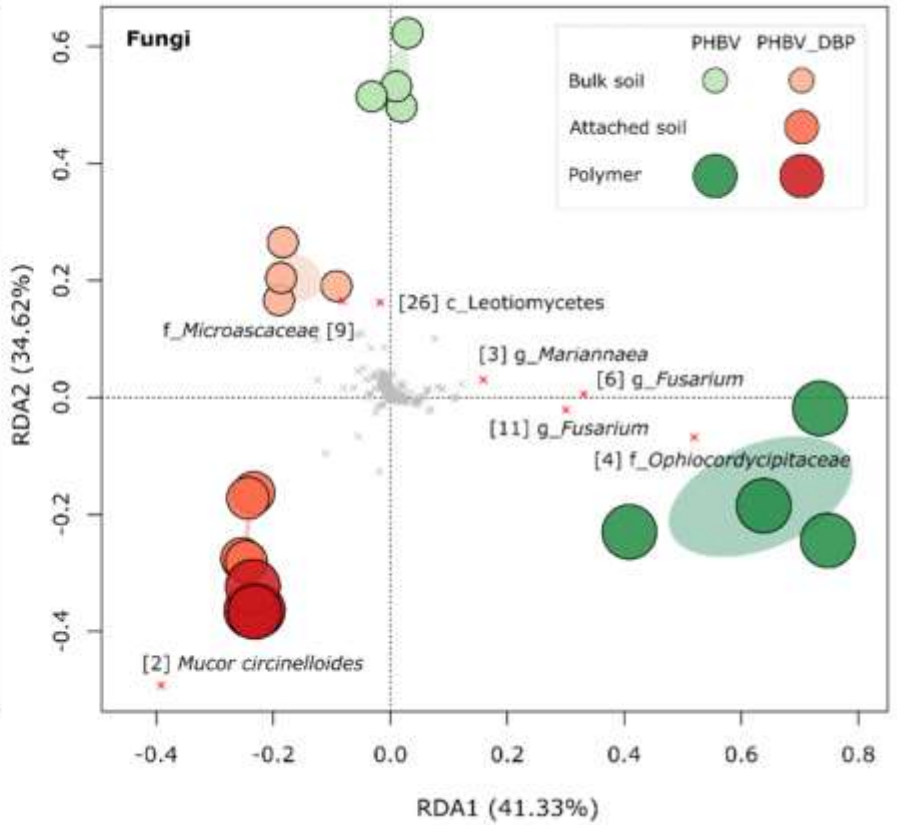
Chan, C.M., et al., *Effect of Toxic Phthalate-Based Plasticizer on the Biodegradability of Polyhydroxyalkanoate.* Environmental Science & Technology, 2022, 56, 17732-17742

Bacterial and Fungal Communities

- Bulk soil differed from polymer-associated communities → Shifts due to polymer presence
- Distinct polymer-associated communities between PHBV and PHBV_DBP







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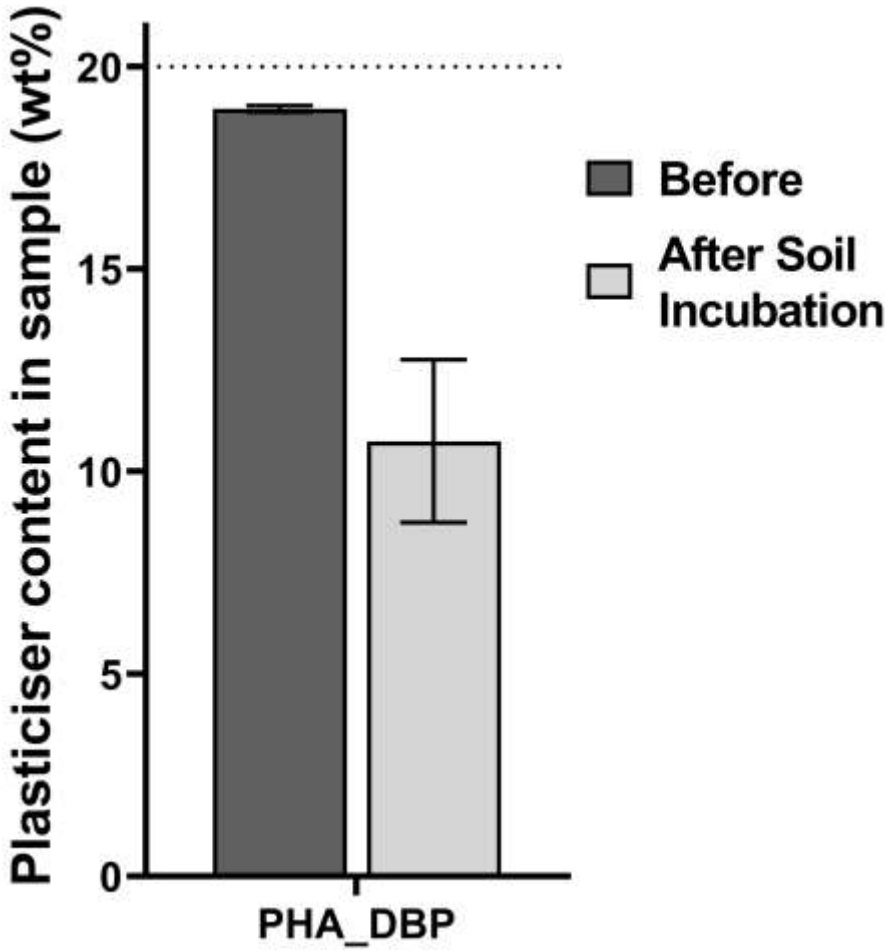
Evidence of Additive Leaching

- Experiment in parellel using a similar but smaller set-up with 5 duplicates
- Consistently, PHBV_DBP showed higher biodegradation rate
- Evidence of DBP migration out of the polymer samples after 3 months of soil incubation from NMR data

PHBV

PHBV_DBP

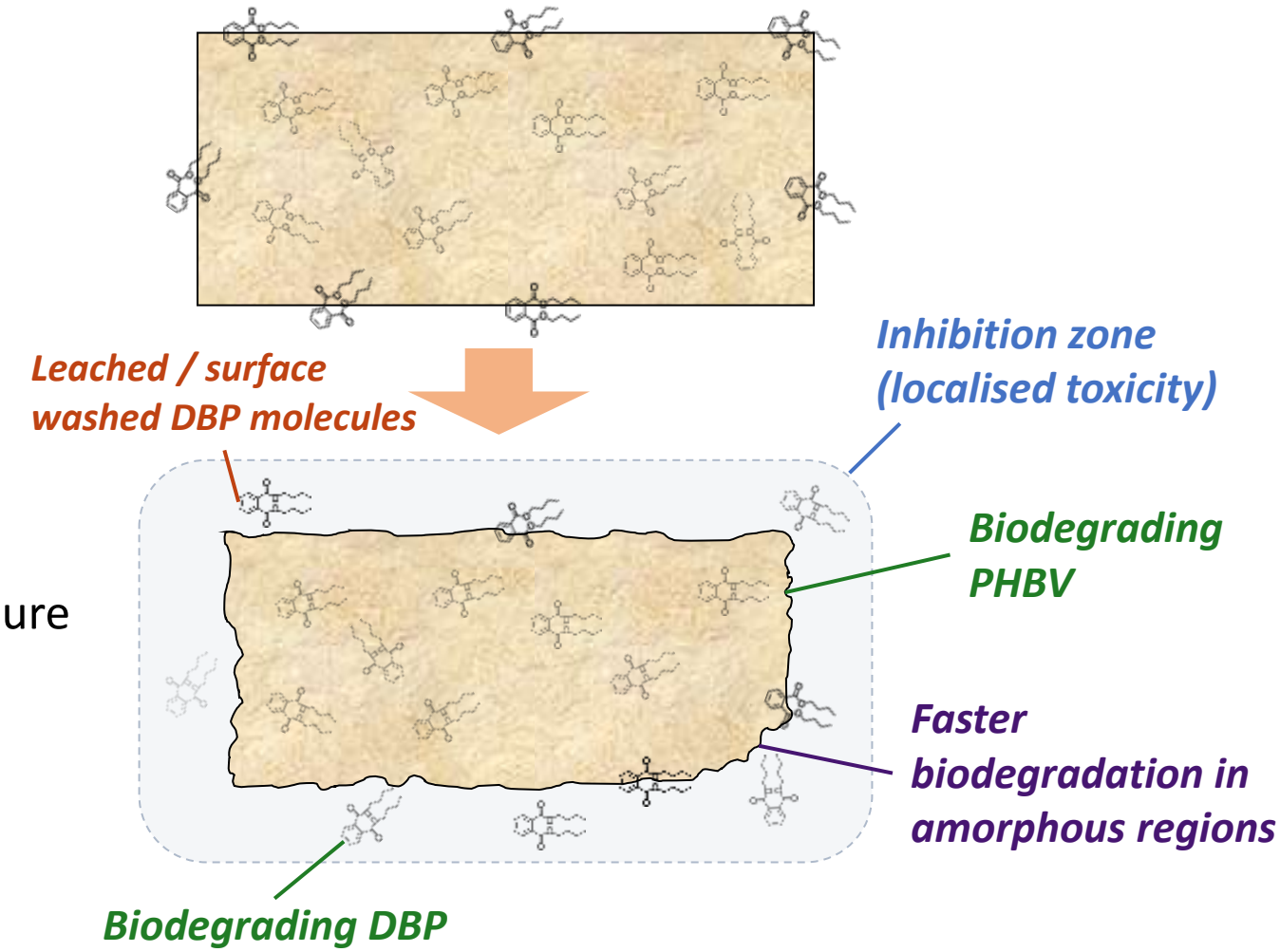
Unpublished data



Unpublished data

Mechanism – Effect of Plasticiser

- **Chemical effects**
  - Leaching of DBP → Inhibition effects
- **Microbial effects**
  - DBP in surrounding soil
    → A shift in local microbial communities
- **Physical effects**
  - Leaching / surface washing of DBP
    → Changes in properties and micro-structure
  - Plasticising effects
    → more rapidly biodegrading amorphous regions



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Conclusion

- Demonstrated the complexity and importance of understanding the effect of additives on biopolymer biodegradation. Controlling factors include:
  - Rate of moisture ingress into the bulk.
  - Changes in polymer properties and micro-structure due to the presence of additives.
  - Leaching/Migration of additives into the surroundings.
  - The nature/properties of the additives
- We are just scratching the surface with these two additive-biopolymer systems and only focusing on the biodegradation angle (ecotoxicity in not within the boundaries of this study)

THANK YOU!

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  - Prof Bronwyn Laycock
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  - Ms. Catherine Hodal (UQ SEES)

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Check out our centre website!!!

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