

Polymères biosourcés et/ou biodégradables :

Éléments de contexte et focus sur les polyhydroxyalcanoates



Prof. Stéphane BRUZAUD

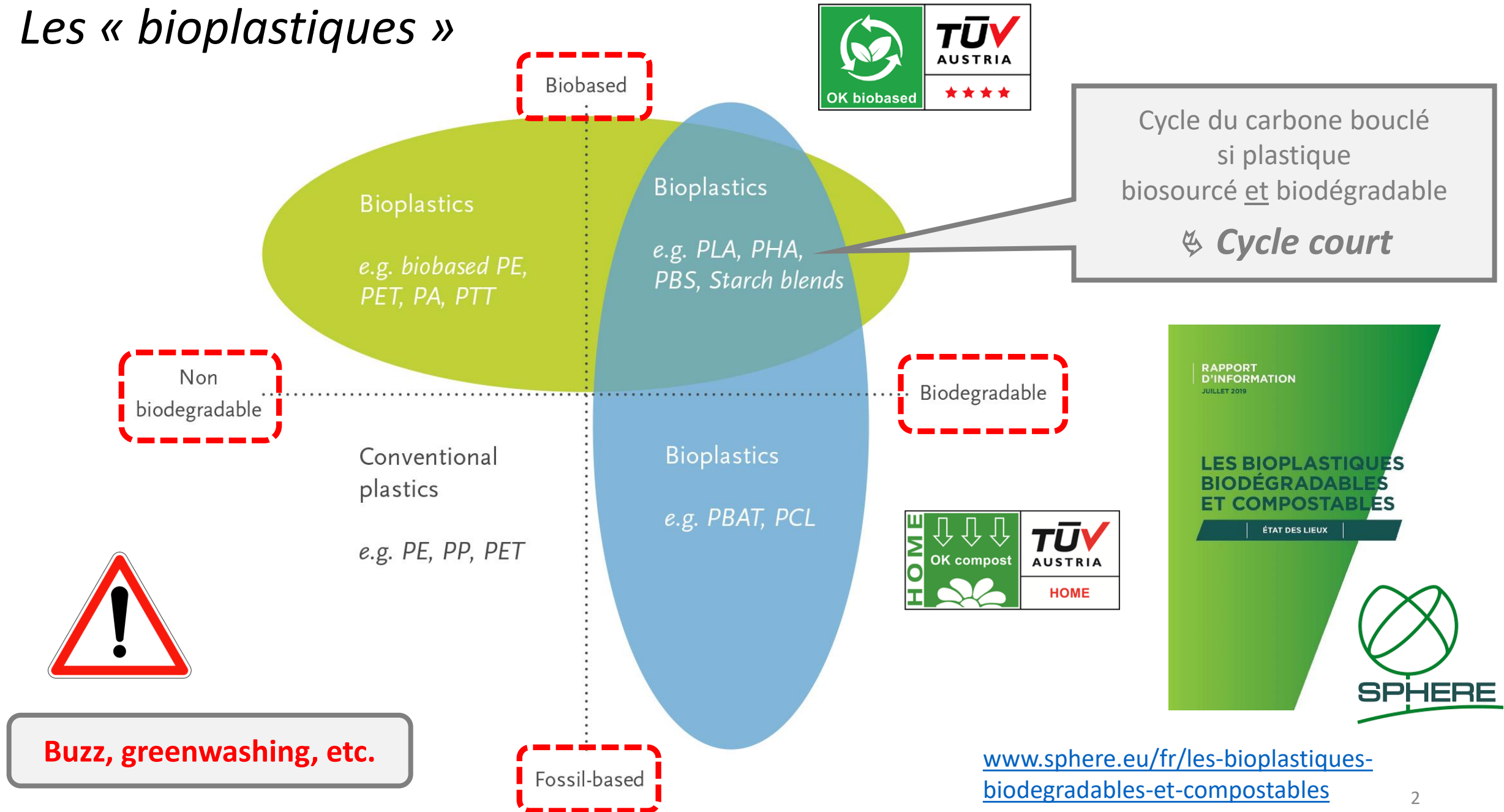
ResearchGate

E-mail : stephane.bruzaud@univ-ubs.fr

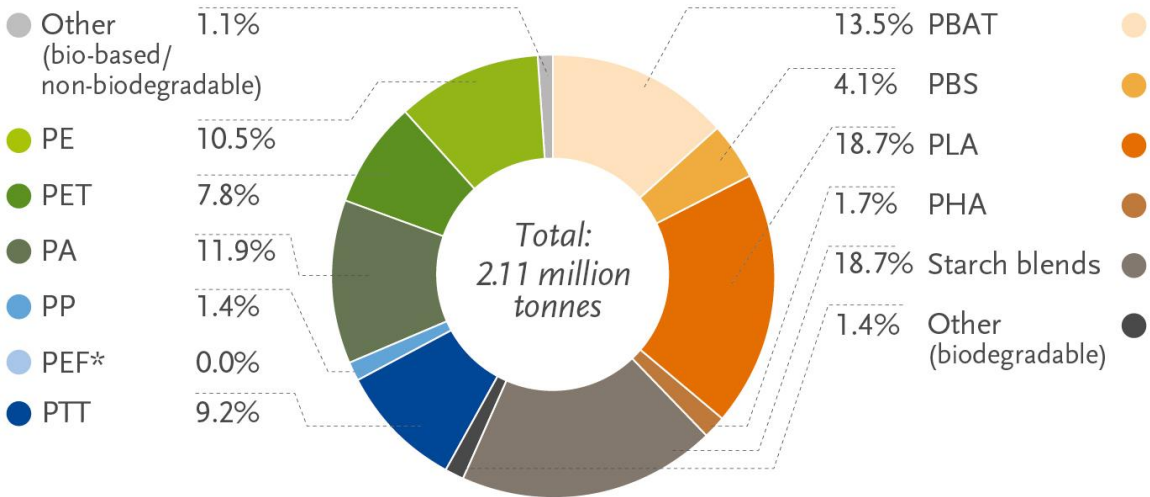
Page web : www.irdl.fr/annuaire/stephane-bruzaud

Webinaire, 29 septembre 2021

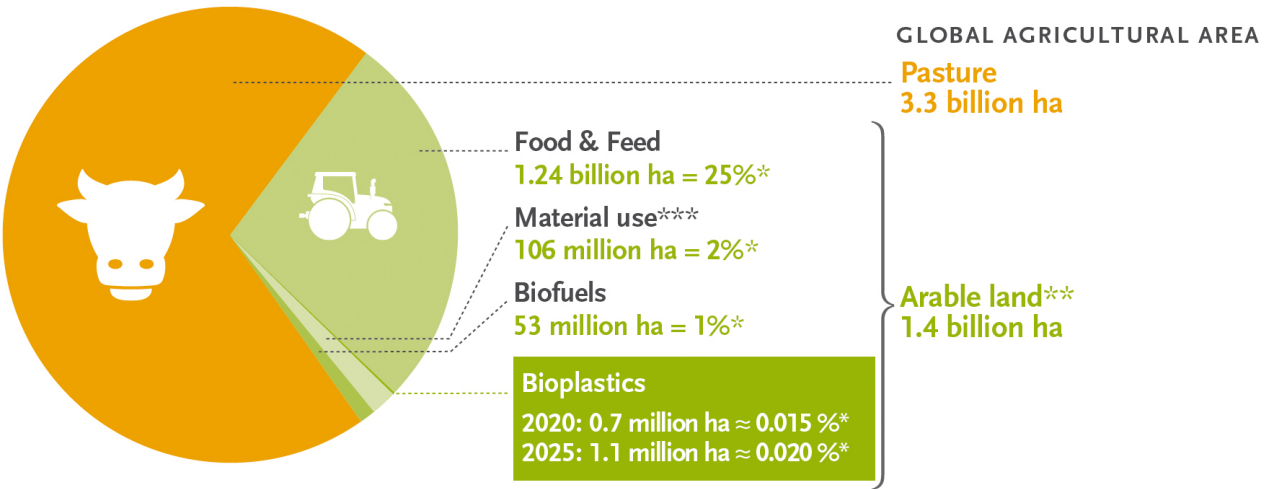
Les « bioplastiques »



Global production capacities of bioplastics 2020
(by material type)



Land use estimation for bioplastics 2020 and 2025



Les différentes générations de biomasse

1^{ère} génération (alimentaire)



Sucres :

Canne à sucre, betterave, etc.

Amidon :

Maïs, blé, pomme de terre, etc.

Huiles végétales :

Soja, palme, tournesol, colza, etc.

2^{ème} génération (non alimentaire)



Biomasse lignocellulosique :

Bois, coproduits ou déchets de l'agriculture ou du bois

Huiles végétales :

Ricin ou résidus de production des autres huiles

3^{ème} génération (non alimentaire ; cultivable hors sol)



Sucres ou huiles produits par des microorganismes :

Microalgues, bactéries, champignons, levures, etc.

Généralités sur les plastiques biosourcés durables

- ❑ **Les polymères biosourcés possédant une structure identique à ceux d'origine pétrochimique** (PE, PET, etc.) ont l'avantage de présenter les mêmes performances techniques et d'utiliser les mêmes technologies de transformation et les mêmes filières de recyclage que ceux-ci.
- ❑ **Des coûts de production encore élevés** liés au coût des matières premières, de leur transformation mais aussi au coût de la recherche en amont et à l'amortissement des investissements.
- ❑ **Des impacts environnementaux encore mal connus.** Une analyse complète sur l'ensemble du cycle de vie des matériaux biosourcés est nécessaire pour établir leur bilan environnemental global. Une attention particulière doit notamment être portée à la phase de production de la ressource (pratiques agricoles et consommations d'intrants (eau, pesticides, engrais, etc.)) et à leur fin de vie.
- ❑ **La gestion en fin de vie des plastiques biosourcés durables reste problématique** au même titre que leurs homologues pétrosourcés.
- ❑ Développer des **plastiques biosourcés éco-conçus**.

Biodégradation : paramètres influents

Facteurs intrinsèques : Matériau

Composition chimique

Surface spécifique

Masse molaire et indice de polymolécularité

Propriétés de surface

(rugosité, balance hydrophile/hydrophobe)

Cristallinité

(degré, taille et organisation des cristallites)

État physique (T_g et T_m) et volume libre

Formulation (mélanges, additifs, renforts, etc.)

Facteurs extrinsèques : Milieu

Composition

(eau douce ou salée, sol, compost, etc.)

Microorganismes (type, nombre, etc.)

Température

Humidité

Oxygène

Rayonnements UV

pH et force ionique

L'étude de la biodégradabilité d'un polymère n'est en aucun cas triviale !

Biodegradable Polymers in Various Environments

According to Established Standards & Certification Schemes

Update
2021

NOTES



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.

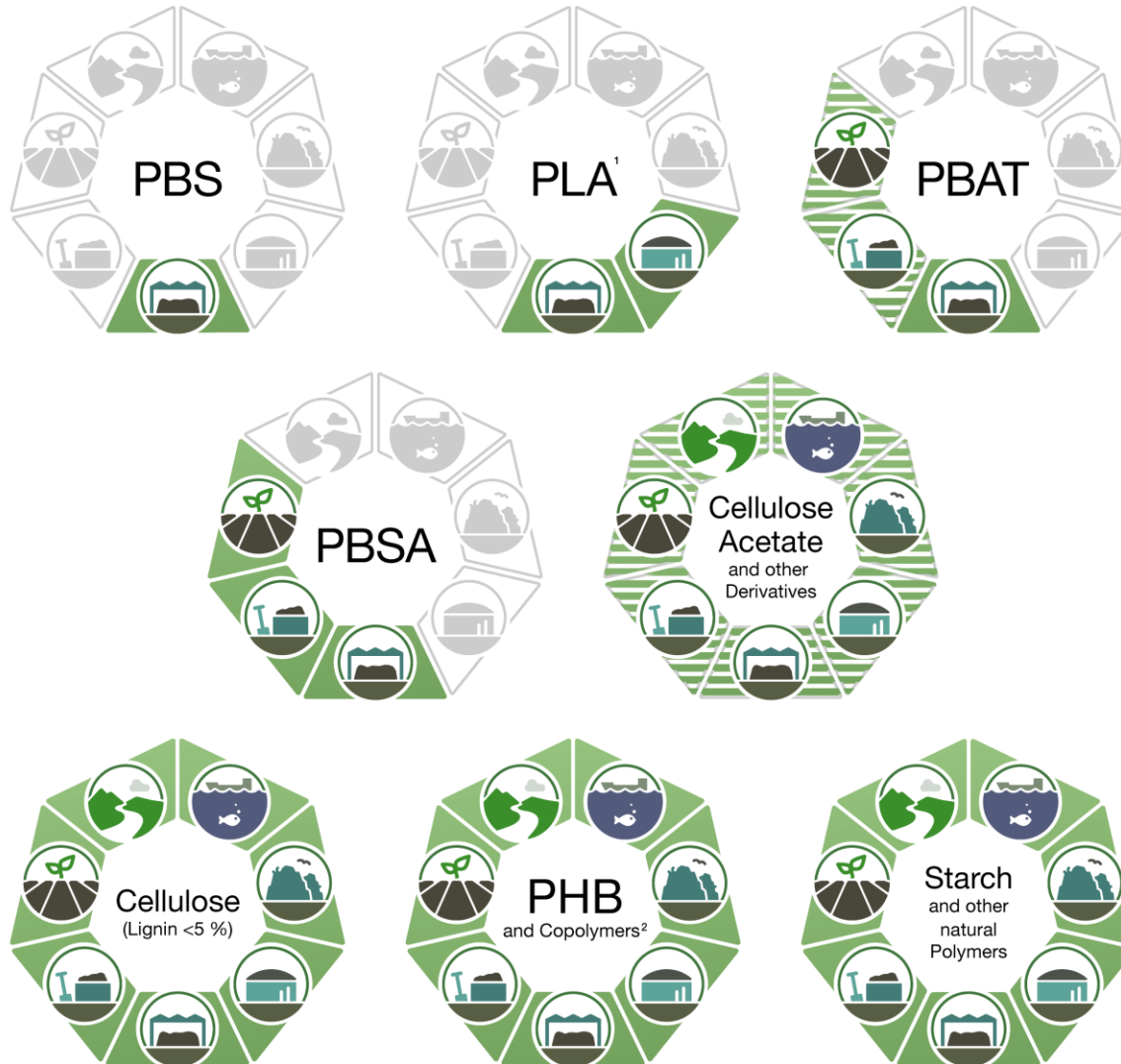
Biodegradability depends on the complex biogeochemical conditions at each testing site (e.g. temperature, available nutrients and oxygen, microbial activity, etc.). Therefore, these generalised claims about biodegradation can only serve as approximations and need to be confirmed by standardised testing 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.

SLOWER BIODEGRADING POLYMERS

The polymers shown in the poster are rapidly biodegraded in the labelled environments, within the time frame of the corresponding standards or certificates. Some biopolymers, such as PBS or PLA in soil and also lignin/wood for virtually all environments, also biodegrade, but (much) more slowly. Full biodegradation can take several years to decades to be achieved. In addition, for some applications with a use phase in a certain environment (e.g. geotextiles), too rapid biodegradation is not desired, as their function should first be given for a few years. However, for these cases no standards exist so far.

¹ PLA is likely to be biodegradable in thermophilic anaerobic digestion at temperatures of 52°C within the time frame mentioned in standards.

² incl. P3HB, P4HB, P3HB4HB, P3HB3HV, P3HB3HV4HV, P3HB3Hx, P3HB3HO, P3HB3HD



ENVIRONMENTS

IMPORTANT TEST CONDITIONS, CERTIFICATION SCHEMES AND STANDARDS

For more details, refer to the original documents.



MARINE ENVIRONMENT

Temperature 30°C, 90 % biodegradation within a maximum of 6 months.
Certification: TÜV Austria OK biodegradable MARINE. Research on standards (both on test methods and requirements) is on-going.



FRESH WATER

Temperature 21°C, 90 % biodegradation within a maximum of 56 days.
Certification: TÜV Austria OK biodegradable WATER. Research on standards (especially on requirements) is on-going.



SOIL

Temperature 25°C, 90 % biodegradation within a maximum of 2 years.
Certification: TÜV Austria OK biodegradable SOIL and DIN CERTCO DIN-Geprüft Biodegradable in Soil. DIN-Geprüft Biodegradable in Soil refers to the European standard EN 17033 for biodegradation in soil and applies to mulch films only.



HOME COMPOSTING

Temperature 28°C, 90 % biodegradation within a maximum of 12 months.
Certification: TÜV Austria OK compost HOME and DIN CERTCO DIN-Geprüft Home Compostable.



LANDFILL

No European standard specifications or certification scheme available since this is not a preferred end-of-life option for biodegradable waste.



ANAEROBIC DIGESTION

Thermophilic 52°C / Mesophilic 37°C
A specific European standard or certification scheme for anaerobic digestion is not yet available. Anaerobic digestion in a biogas plant is mentioned in EN 13432 and EN 14995: 50 % biodegradation within two months, usually followed by aerobic digestion.

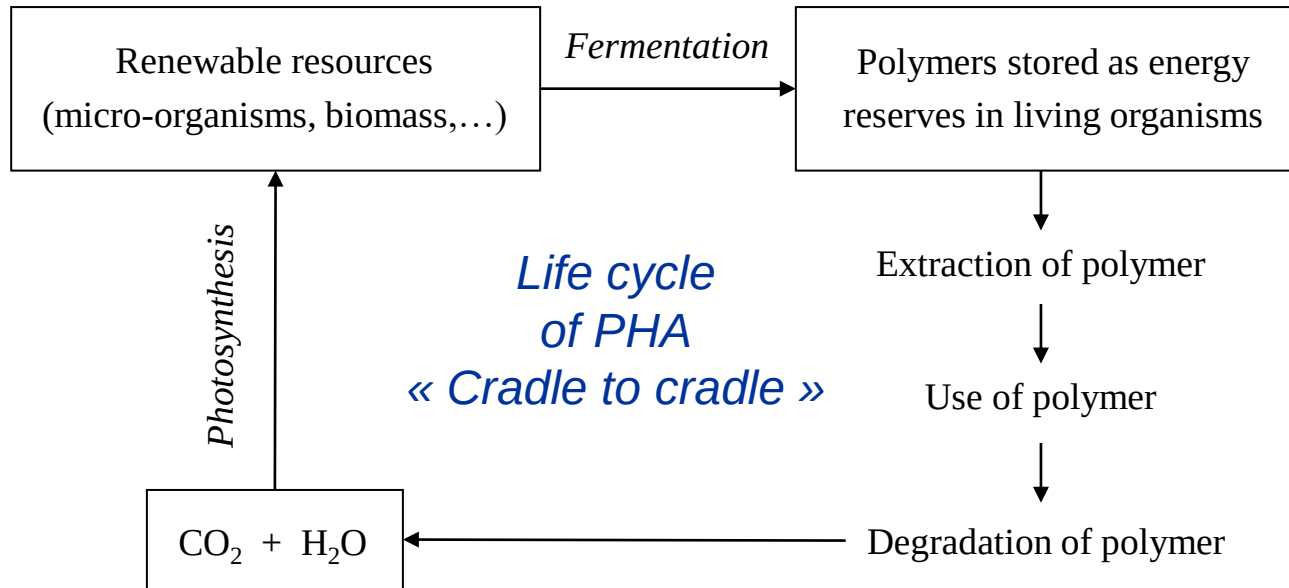


INDUSTRIAL COMPOSTING

Temperature 58°C, 90 % biodegradation within a maximum of 6 months.
Certification: TÜV Austria OK compost INDUSTRIAL, DIN CERTCO DIN-Geprüft Industrial Compostable and both „Seedling“. EN 13432 and EN 14995 are the European reference standards and the basis of these certification schemes.

<https://renewable-carbon.eu/publications/pro-duct/biodegradable-polymers-in-various-environments-according-to-established-standards-and-certification-schemes-graphic-png/>

The polyhydroxyalkanoates (PHA)

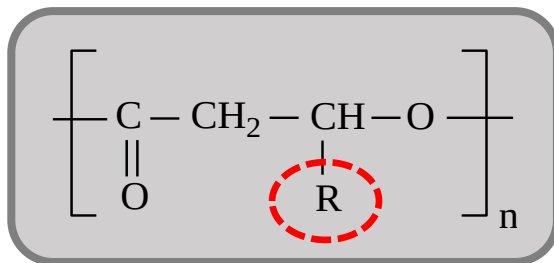


Biotechnology approach

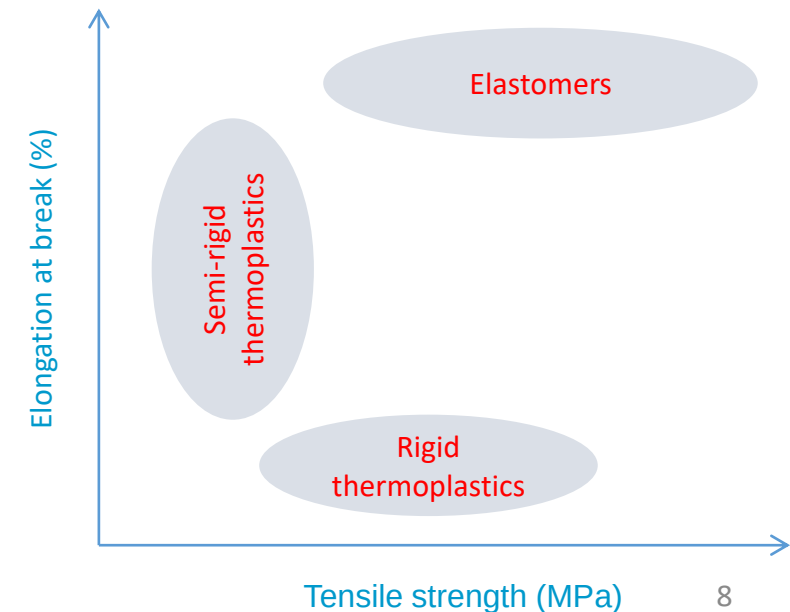


PHA

Biobased and biodegradable
(+ biocompatible)

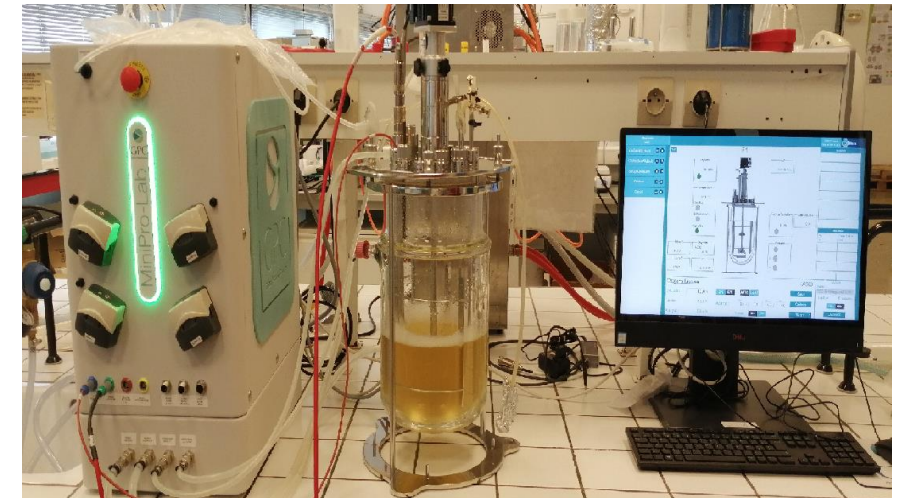
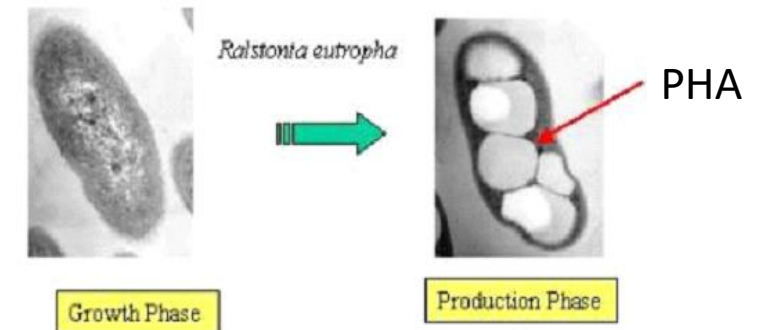
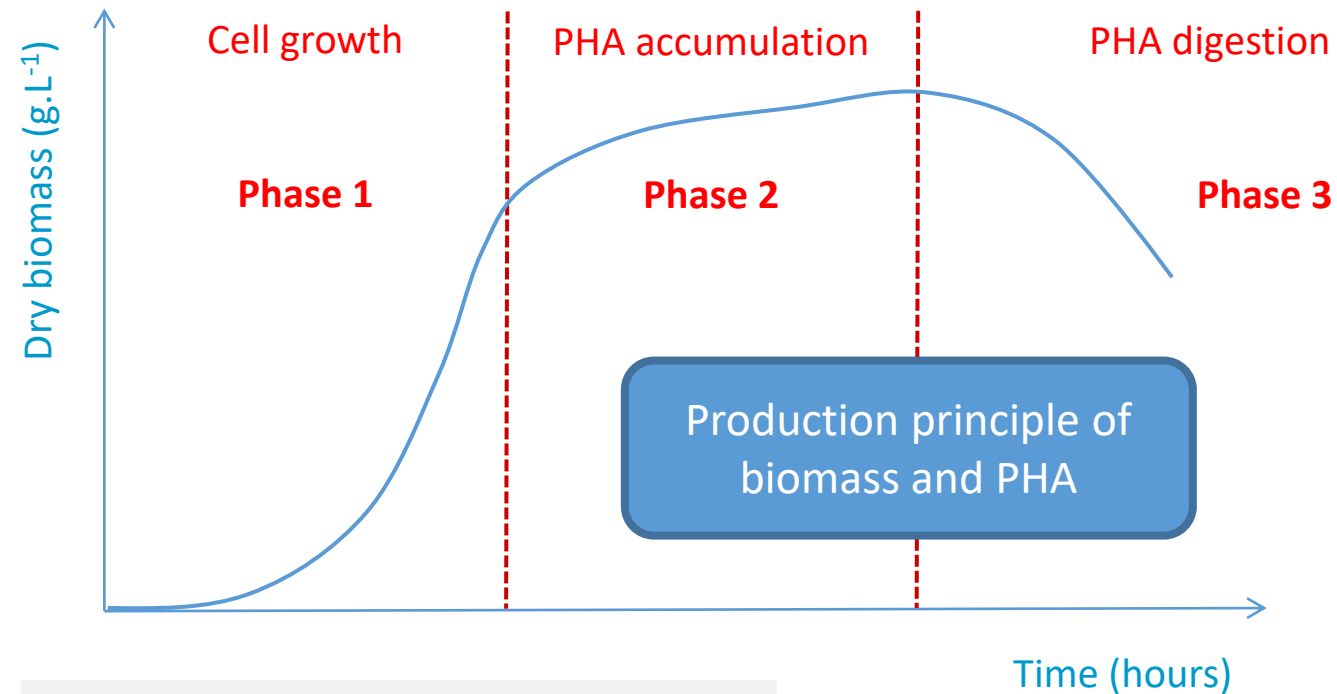


PHA	R	Unit
scl-PHA	CH ₃	HB
	C ₂ H ₅	HV
mcl-PHA	C ₃ H ₇	HHx
	C ₄ H ₉	HHp
	C ₅ H ₁₁	HO



The PHA biosynthesis

- ❑ The carbon source (sugars, fatty acids or vegetable oils) influences the PHA structure.
- ❑ After few growth hours, the bacteria begin to accumulate PHA in their cytoplasm as energy reserves.
- ❑ Parameters to be monitored: temperature, pH, stirring, oxygen pressure, concentrations, etc.



PROGRAMS

BIOCOMBA (2010-2011)

PHAPACK (2012-2014)

BLUECOPHA (2015-2018)

Challenge: Production of bioplastics using local resources

Technical validation at:

- Pilot scale (50 L (10 runs) and 1000 L)
- Industrial pilot (30 000 L)

 europlastiques

 **PROOF OF CONCEPT**

ADEME



Agence de l'Environnement
et de la Maîtrise de l'Energie



A sustainable and
environmentally
friendly process



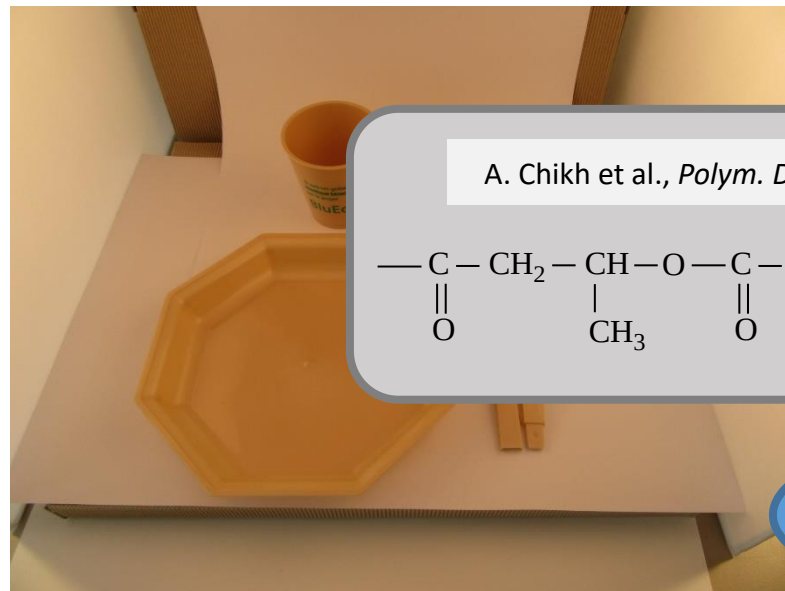
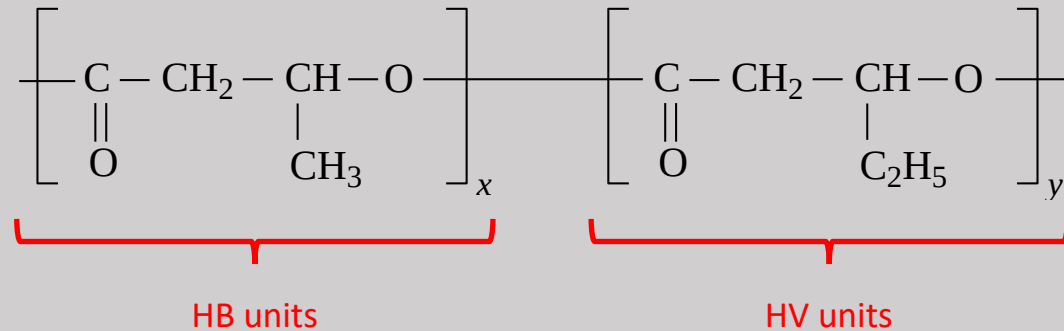
New value
chain

et al., *J. Microbiol. Biotechnol.* **2015**
Crops Prod. **2016**

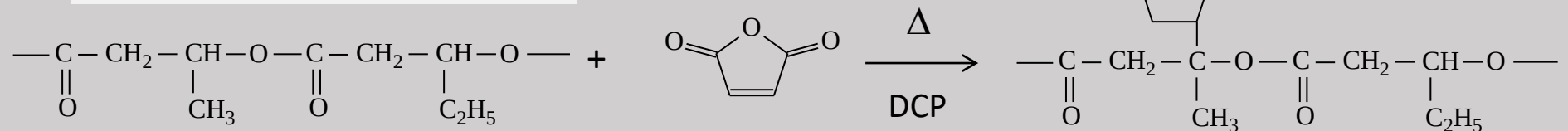
Short chain length PHA



P. Lemechko et al., *Int. J. Biol. Macromol.* **2019**



A. Chikh et al., *Polym. Degrad. Stab.* **2017**



scl-PHA

PHBHV (3% HV)

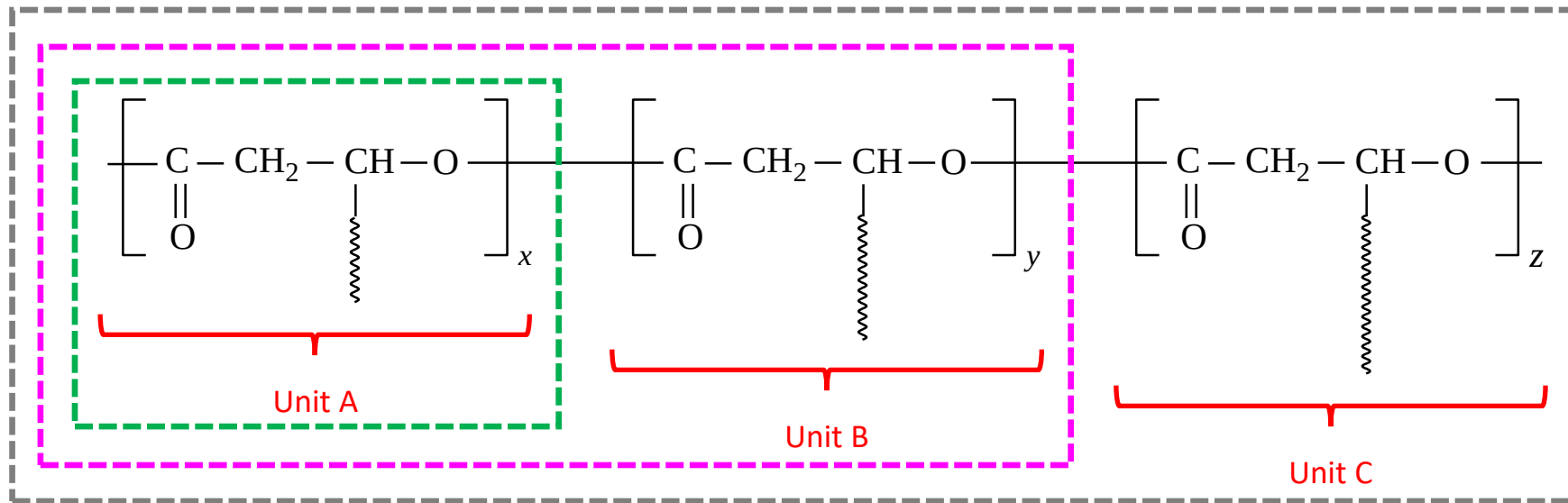
PHBHV (27% HV)

~ 40 μm

PHBHV (15% HV)

PHBHV (43% HV)

Tailor-made medium chain length PHA



<i>mcl</i> -PHA	T _g (°C)	ΔH _m (J.g ⁻¹)
PHHp	-30	-
PHOHHx	-35	15
PHOHU	-44	7
PHBHV (Y1000P)	+8	100

☐ Solubility in eco-friendly solvents

<i>mcl</i> -PHA: homo-, co- and ter-polymers		
A	Poly(3-hydroxyheptanoate)	PHHp
AB	Poly(3-hydroxybutyrate-co-3-hydroxyheptanoate)	PHBHHp
AB	Poly(3-hydroxyoctanoate-co-3-hydroxyhexanoate)	PHOHHx
ABC	Poly(3-hydroxyoctanoate-co-3-hydroxydecanoate-co-3-hydroxydodecanoate)	PHOHDHDD
ABC	Poly(3-hydroxyoctanoate-co-3-hydroxynonanoate-co-3-hydroxyundecenoate)	PHOHNHU

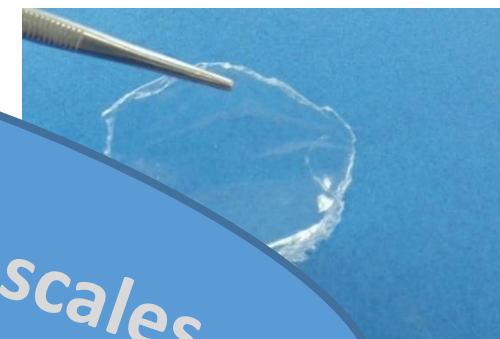
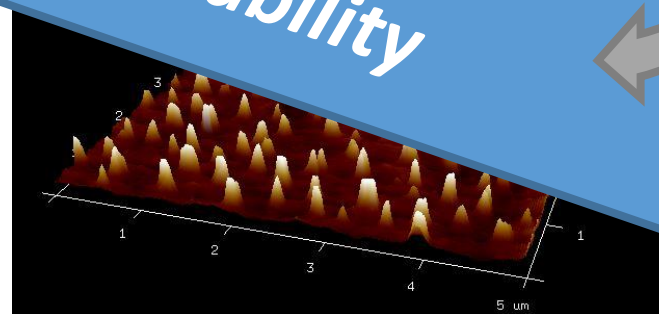
Exa

Relationships between:

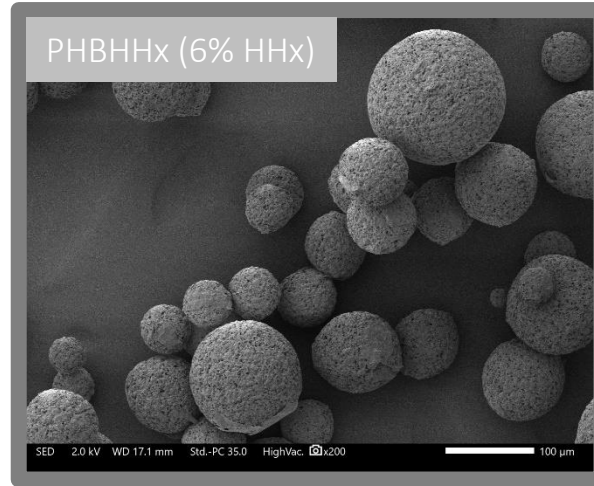
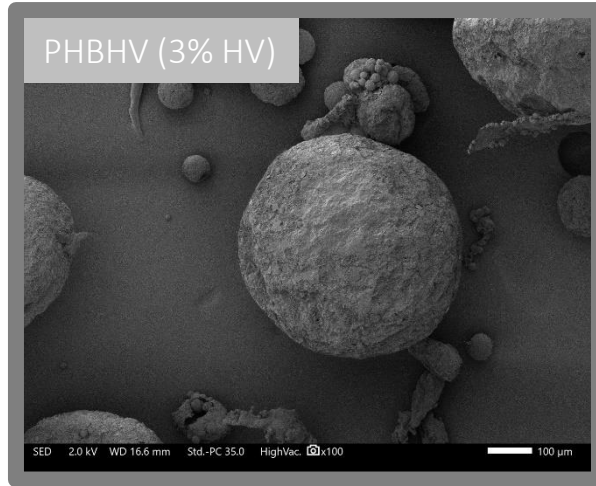
Chemical structure
Morphology

Functional properties
(Bio)degradability

At different scales



Elaboration of PHA-based microbeads

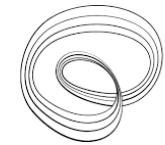


BIOBILLES



Région
BRETAGNE

LESSONIA
cosmetics + ingredients



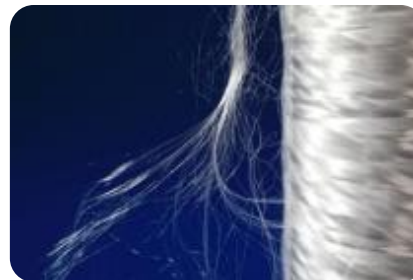
**Biotech
& Santé**
BRETAGNE

PHA	Size (μm)	Circularity	Rugosity Ra (nm)	Modulus (MPa)	Hardness (MPa)	ΔH_m (J.g ⁻¹)
PHBHV (3% HV)	100	0.91	122	6800	260	97
PHBHHx (6% HHx)	75-100	0.93	65	2800	95	56
PHBHHx (11% HHx)	75-100	0.90	45	1700	65	40

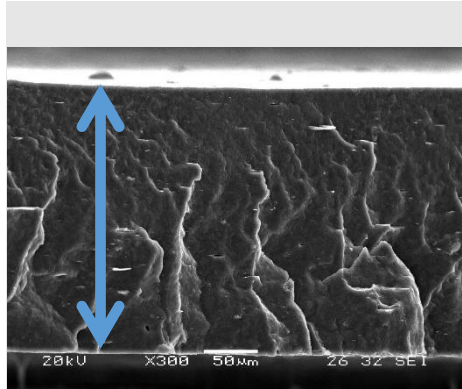
Degradation in natural seawater



Kernevel harbour
(Larmor-Plage [56])



Degradation in natural seawater



$t = 0$

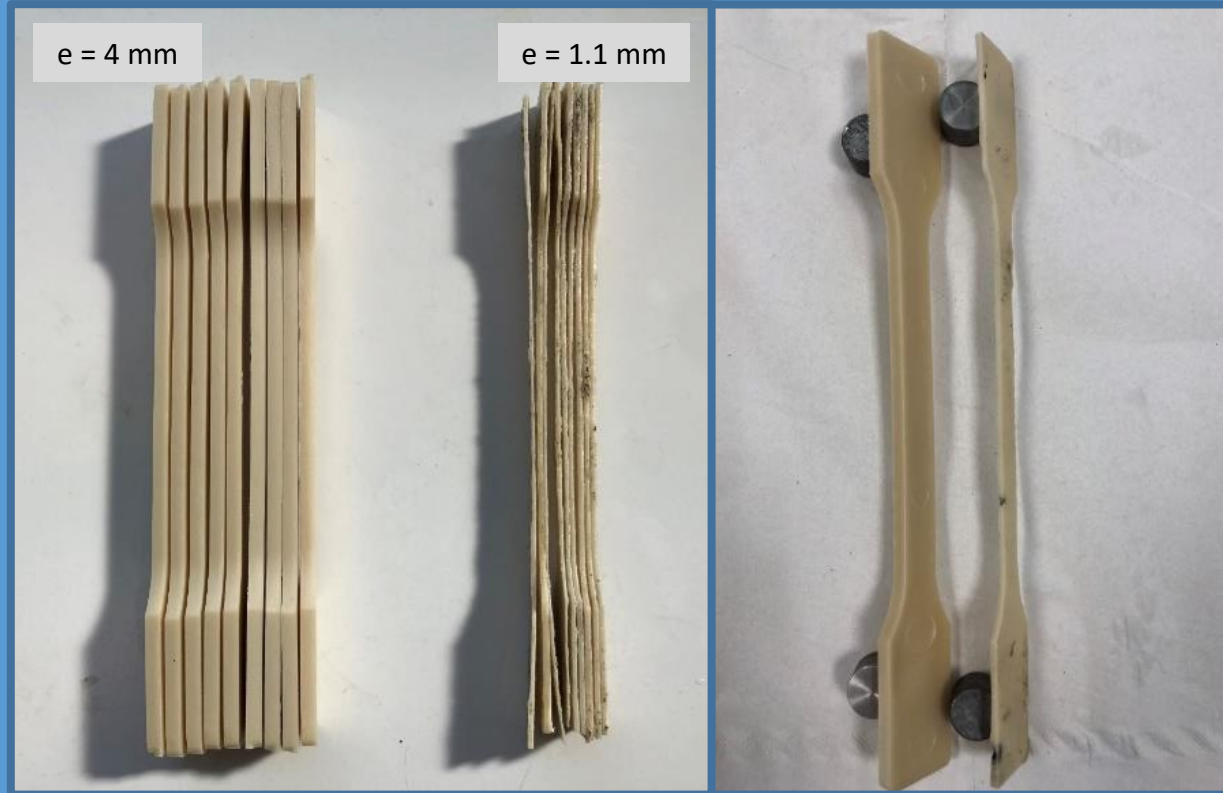
$e = 200 \mu\text{m}$

P

PHBHV specimens aged **78 months** (6.5 years) in natural seawater

$e = 4 \text{ mm}$

$e = 1.1 \text{ mm}$



M. Deroiné et al., *Polym. Degrad. Stab.* in preparation

PHV films

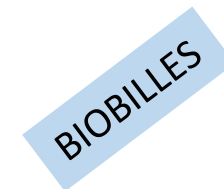
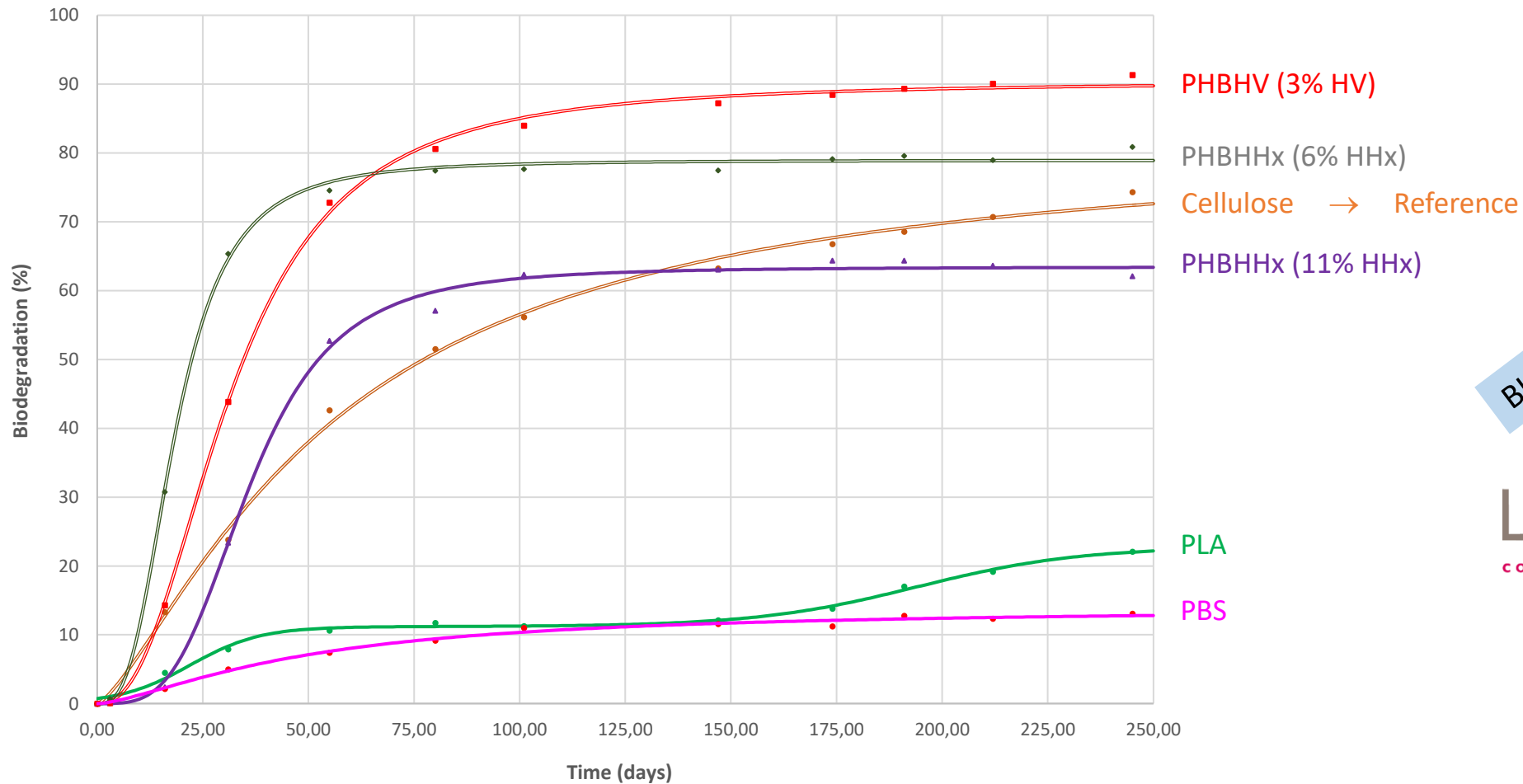
Deroiné et al.
J. Polym. Sci. Part A: Polym. Chem. **2015**

- ☐ High mass loss
- ☐ Little change in thickness
- ☐ Little change in tensile strength

Biodegradation in marine environment

C. Volant et al., *J. Polym. Env.* submitted

- PHA powders in seawater + sediments at 25°C (NF EN ISO 19679 standard)

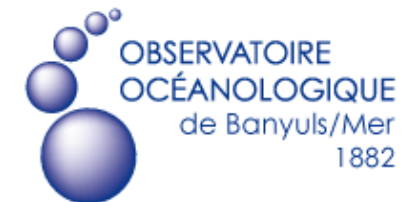


Biodegradation in marine environment

PHA	MW (g.mol ⁻¹)	T _g (°C)	T _m (°C)	ΔH _m (J.g ⁻¹)	Biodegradation
PHBHV (3% HV)	340 000	5	175	100	+++
PHBHHx (6% HHx)	112 000	1	143	47	++
PHBHHx (11% HHx)	123 000	0	130	38	+



Ph.D. G. Derippe, UBS 2020-2023
Supervisors: S. Bruzard & J.F. Ghiglione



Relationships chemical structure-morphology-properties in the PHA:
Influence on the biodegradability in marine medium

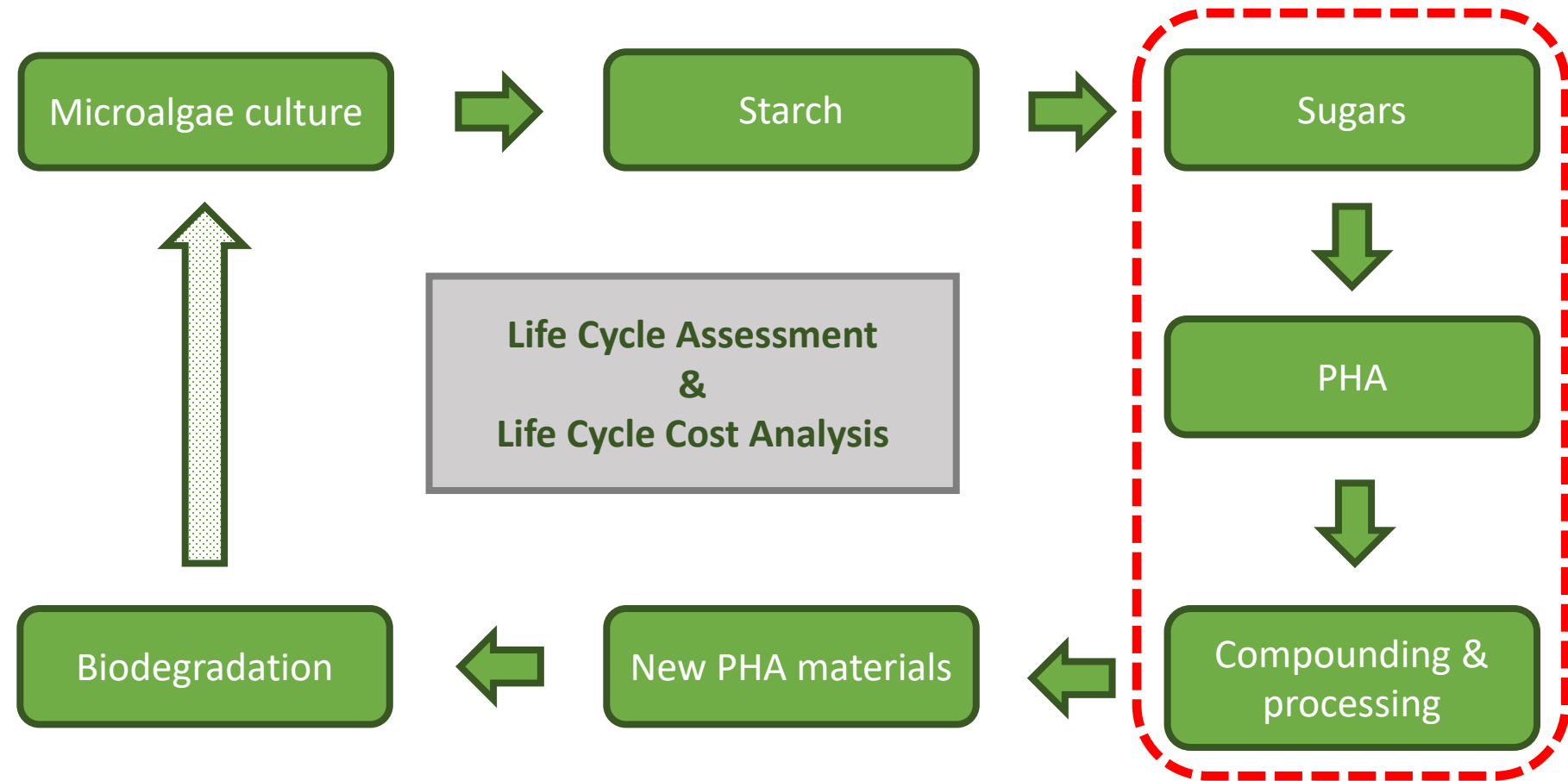
Towards polymers with planned (bio)degradation?



- ❑ **16 EU partners** (7 countries)
 - 1 academic
 - 1 innovation cluster
 - 4 RTO
 - 4 large companies
 - 6 SME
- ❑ Project duration **42 months**
- ❑ Total cost **€ 6.4M**

More information:

<https://nenu2phar.eu>
cordis.europa.eu/project/id/887474/fr



Kick-off meeting-15th September, 2020 , SKYPE meeting

For a sustainable and european value chain of PHA-based materials for high-volume consumer products

Which applications for PHA?

❑ Packaging: Low value added sector

- ❖ No real application identified in packaging
 - TIANAN Y1000P 8 to 12 €/kg (bag of 25 kg)

❑ Cosmetics, biomedical, 3D printing: High value added sectors

- ❖ Cosmetics: Microbeads, functional ingredients, etc.
- ❖ Biomedical: Suture thread, medical devices, controlled-release systems, etc.
- ❖ 3D printing: As an additive for improvement in the PLA robustness
Filaments from 30 to 70 € (1 kg)



PLA/PHA 1.75 MM

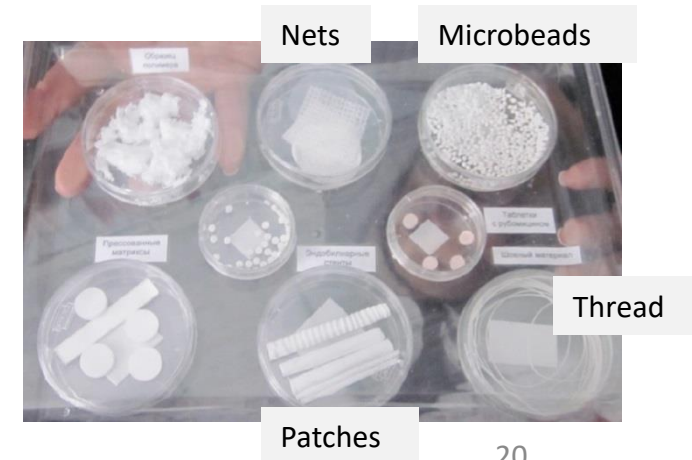


PLA/PHA 2.85 MM



PLA/PHA 2.85 MM

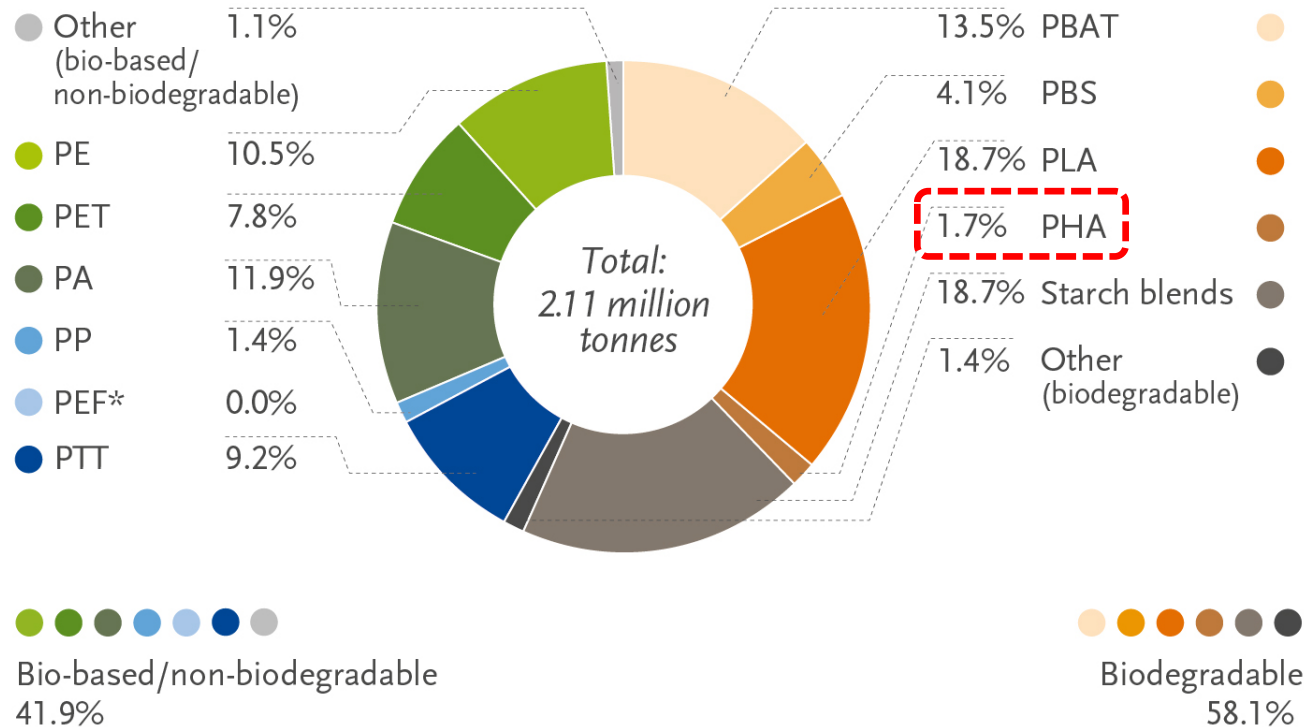
Warning towards announcement effects
Evolution in the legislation
Business model



What future for PHA?

<https://www.european-bioplastics.org>

Global production capacities of bioplastics 2020 (by material type)

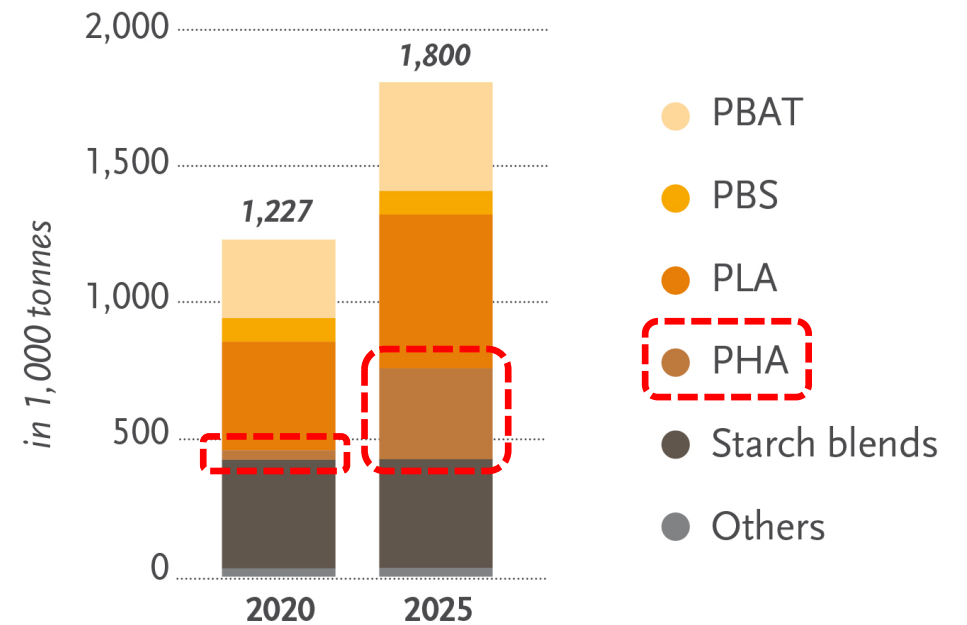


*PEF is currently in development and predicted to be available in commercial scale in 2023.

Source: European Bioplastics, nova-Institute (2020)

More information: www.european-bioplastics.org/market and www.bio-based.eu/markets

Biodegradable bioplastics 2020 vs. 2025



Source: European Bioplastics, nova-Institute (2020)

More information: www.european-bioplastics.org/market and www.bio-based.eu/markets

Top 10 Emerging Technologies 2019



COMMITTED TO
IMPROVING THE STATE
OF THE WORLD



Less than 15% of the world's plastic is recycled, with the rest incinerated, abandoned or sent to landfill. Biodegradable plastic offers a promising solution.

A breakthrough idea promotes the circular economy by using resources from biomass, without using crops that could otherwise be used for food.

1. Bioplastics for a Circular Economy
2. Social Robots
3. Tiny Lenses for Miniature Devices
4. Disordered Proteins as Drug Targets
5. Smarter Fertilizers Can Reduce Environmental Contamination
6. Collaborative Telepresence
7. Advanced Food Tracking and Packaging
8. Safer Nuclear Reactors
9. DNA Data Storage
10. Utility-Scale Storage of Renewable Energy

Pour en savoir plus...

Plus d'informations :

Email : stephane.bruzaud@univ-ubs.fr

Page web : www.irdl.fr/annuaire/stephane-bruzaud

N° 427-428 MARS-AVRIL 2018



LA BIOTECHNOLOGIE AU SERVICE DE LA CHIMIE POUR OBTENIR DES POLYMÈRES BACTÉRIENS BIODÉGRADABLES

Pagination : 60-65

Sous-thème : Chimie et développement durable

Mots-clés : Chimie durable, polyhydroxyalcanoates (PHA), biosynthèse, ressources renouvelables, biodégradation.

Par Stéphane Bruzaud , Pierre Lemechko



TECHNIQUES
DE L'INGÉNIEUR

Date de publication :
10 août 2021

Réf. : **CHV4039**

Polyesters biosourcés et/ou biodégradables

De l'élaboration à la fin de vie

par **Stéphane BRUZAUD**

*Professeur des Universités
Université Bretagne Sud, Institut de Recherche Dupuy de Lôme,
UMR CNRS 6027, Lorient, France*