JCAT 53 – 53èmes Journées de Calorimétrie et d'Analyse Thermique - 22-24 mai 2023 PALAISEAU (France)

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Monitoring the degradation status of biodegradable polymers by assessing thermal properties

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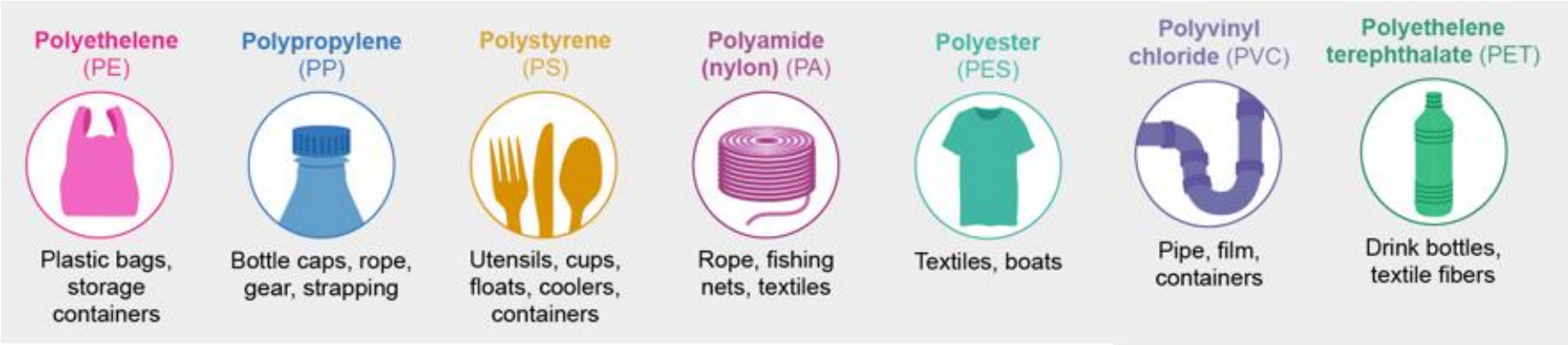
A tremendous demand for plastics



Plastic wastes accumulation => environmental damage

Terrestrial

Marine

Mechanisms involved in biodegradation

successive or concomitants mechanisms

Biodegradation = $\sum$ [**Physical** | **Chemical** | **Biological**]

Microorganisms

$CO_2 + H_2O + ATP$

aerobic

$CH_4 + CO_2 + H_2O + ATP$

anaerobic

Biodegradable

Not biodegradable

FRAGMENTATION ⇨ **DEGRADATION** ⇨ **BIO-ASSIMILATION**

Reduction of material in fragments or particles without major modification of molecular weight and chemical structure
=> Last stage = ***disintegration***

Biotic phenomena via enzymes (hydrolysis and oxidation) and abiotic (photo-degradation, hydrolyse, oxidation, etc.) leading to a significant ***decrease of molecular weight***

Integration by microorganisms of molecular degradation products oligomer, monomer and ***conversion in biomass, water and mineral carbon CO_2 and/or methane CH_4***

MACROSCOPIC → *MICROSCOPIC* → *MACROMOLECULAR* → *MOLECULAR*

Understanding of the main **physical-chemical properties**

that affect their biodegradation rate

to

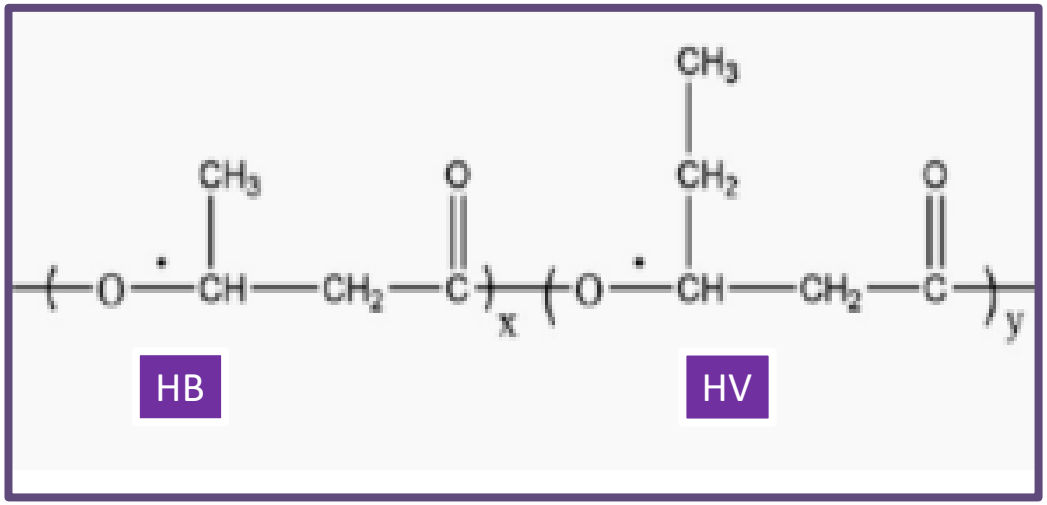
Identify **key limiting factors** driving biodegradation

by combining different methodological approaches

PHBV

Polyhydroxybutyrate-co-valerate

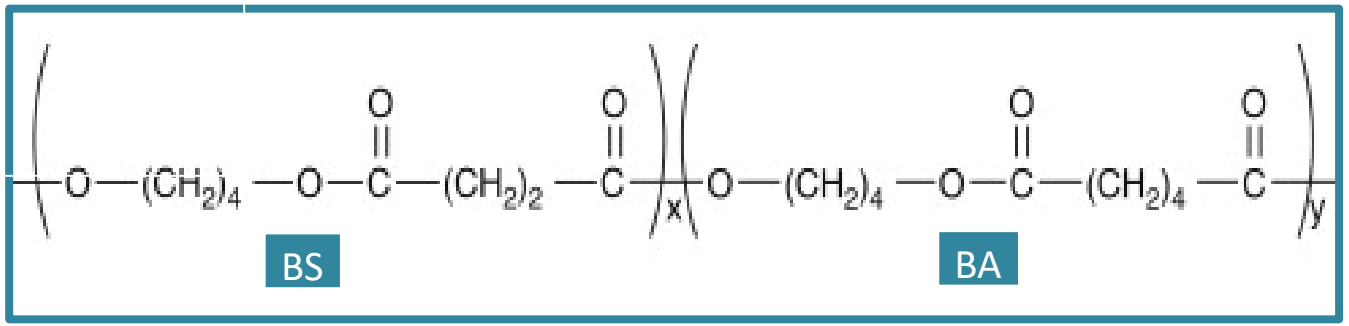
PHI 002 (NaturePlast)
1-3% mol HV
Xc = 54 % (DSC)
Mn ≈ 94 000 g/mol



PBSA

Polybutylene succinate-co-adipate

PBE 001 (NaturePlast)
21% mol BA
Xc = 47% (DSC)
Mn ≈ 44 000 g/mol



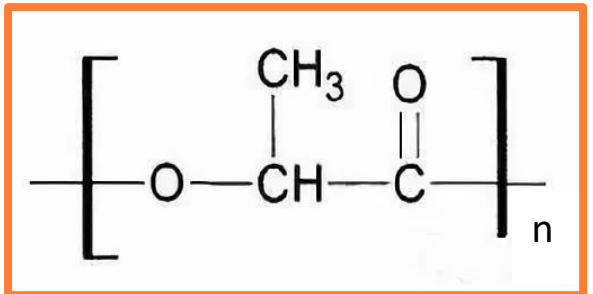
PLA

Polylactic acid

Natureworks
Amorphous
d = Ø
Mn ≈ 75 311 g/mol

Total Corbion
Semi-crystalline
d = 31.13 % (DSC)
Mn ≈ 82 960 g/mol

Lyspackaging
Semi-crystalline
d = 25.52 % (DSC)
Mn ≈ 103 760 g/moll



PHBV

PBSA

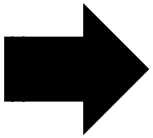
Biodegradation process in composting conditions


Pieces of film


100 days


50% humidity


58°C

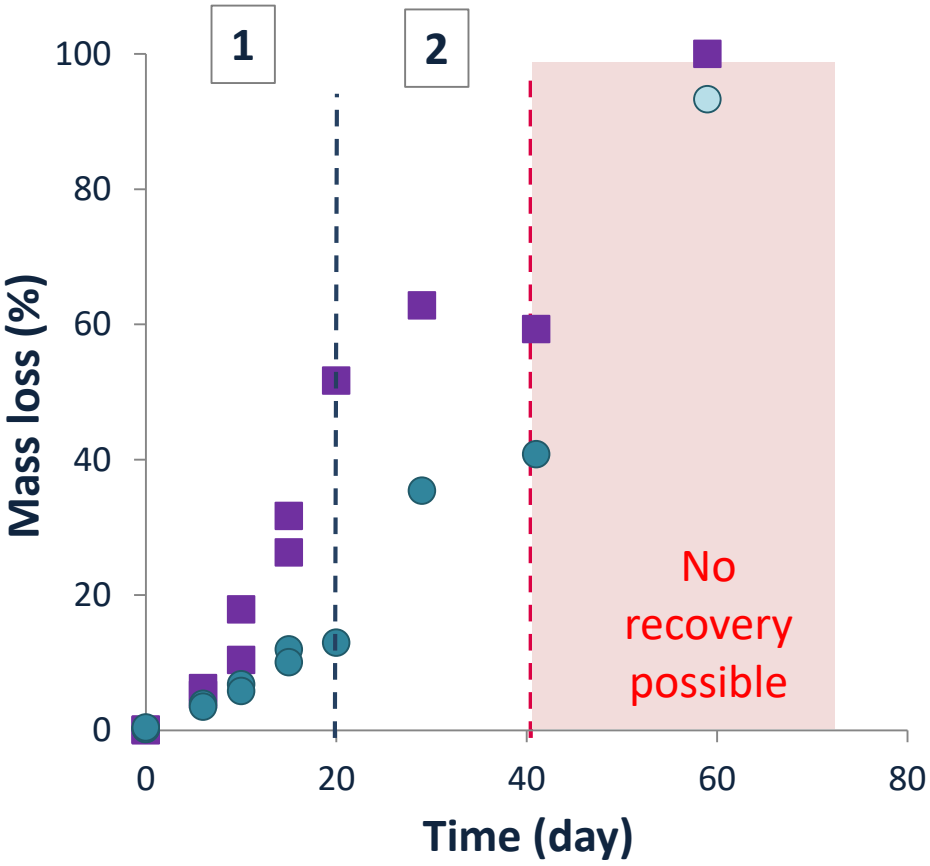


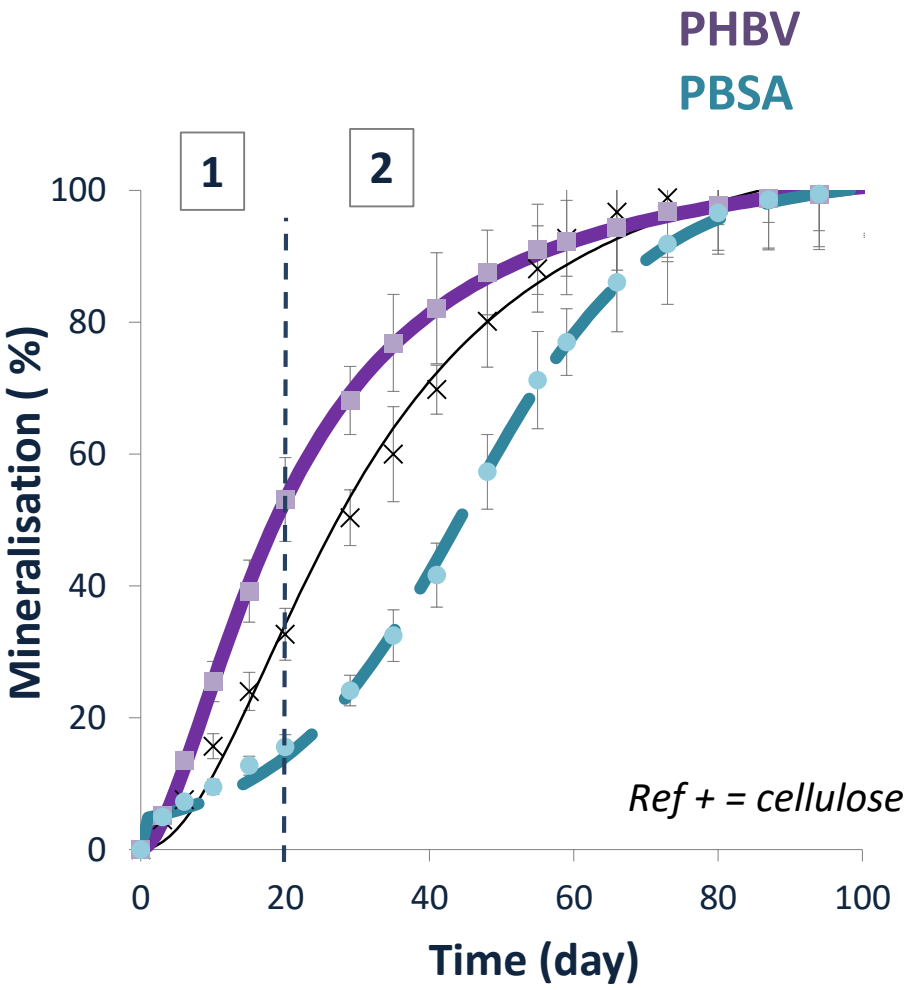
sampling during the biodegradation processs

Physical-Chemical Analysis

- Mass loss (weighting)
- Mineralisation (respirometry)
- Surface erosion (SEM)
- Surface hydrolysis (FTIR)
- Molar Mass (SEC)
- Tg, Xc (DSC)

Biodegradation in industrial composting conditions (58°C)

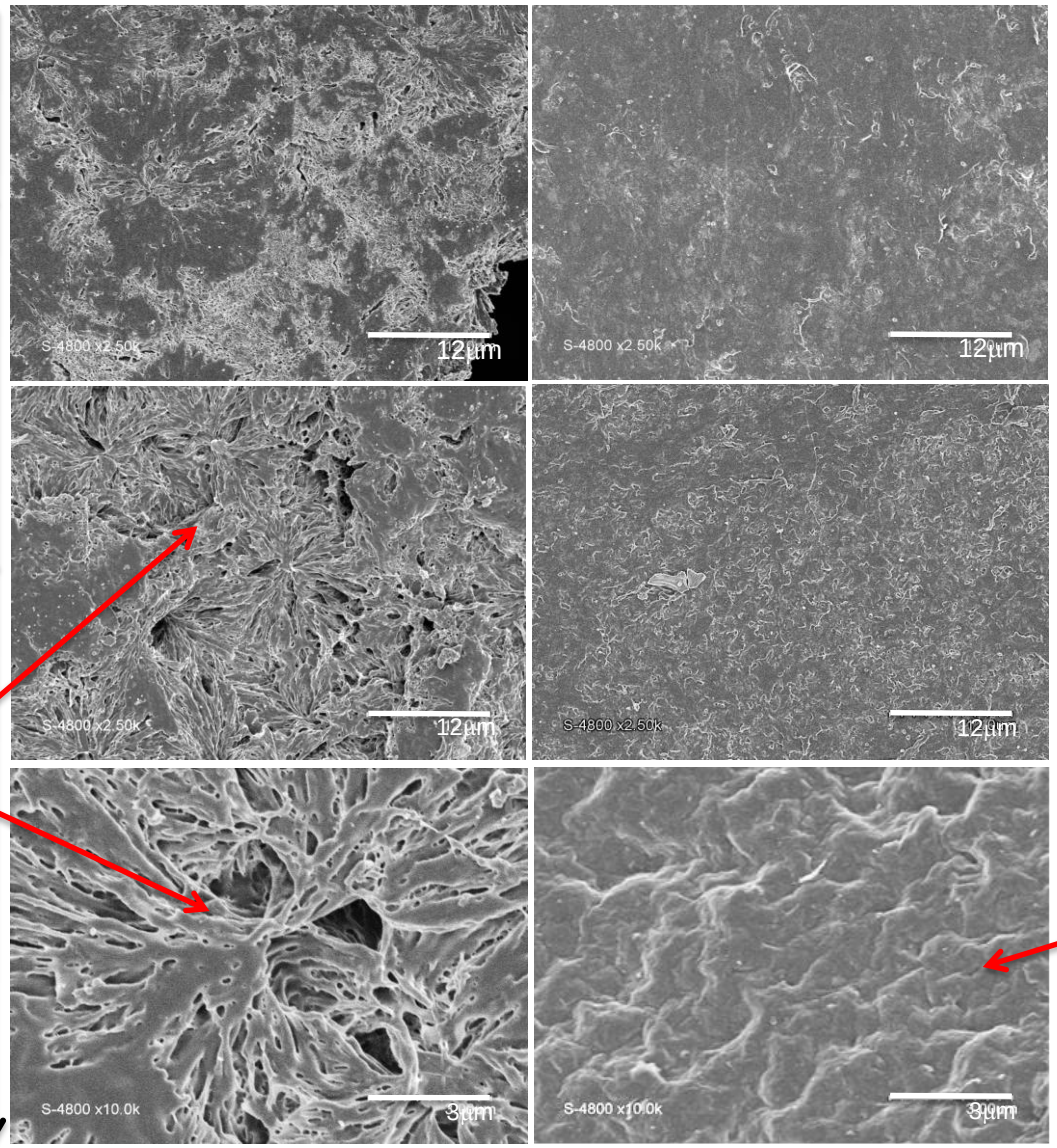




Phase 1 : PHBV > PBSA

Phase 2 : PHBV < PBSA

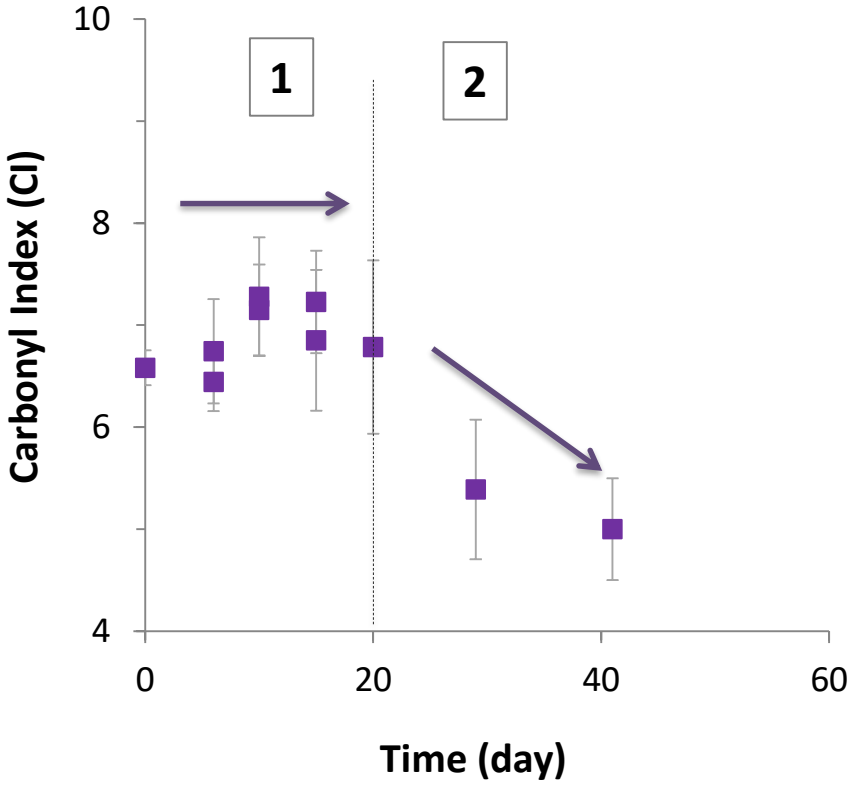
PHBV vs PBSA


Degradation time (day)
6
Significant erosion/etching
10
spherulites
20
flat layers of crystal
Erosion delayed
S-4800 x2.50k
12μm
S-4800 x10.0k
3μm

FTIR

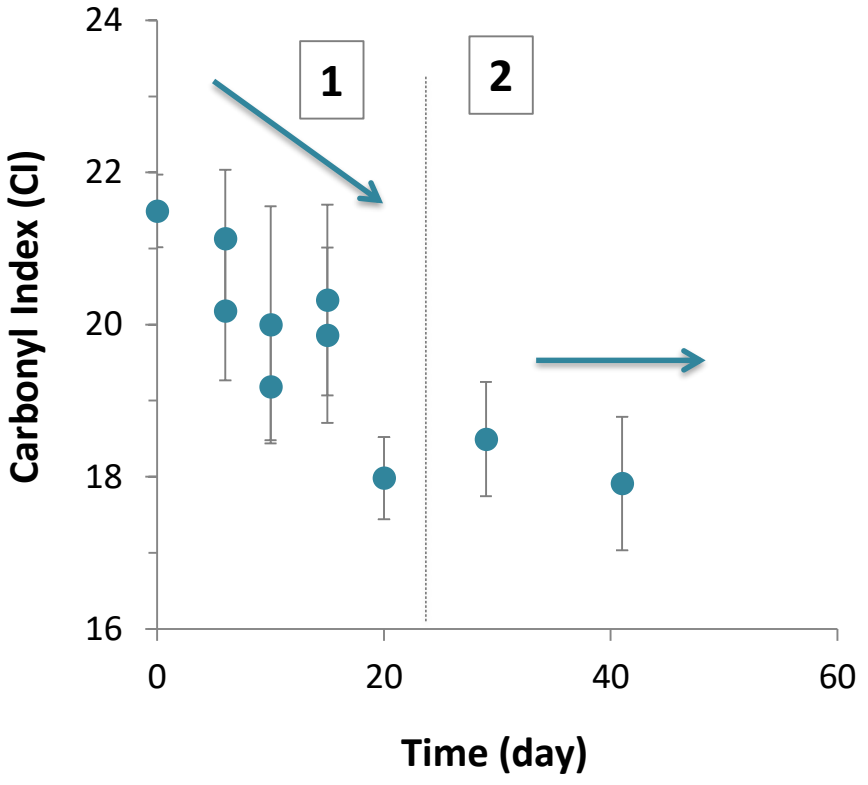
PHBV

$$CI = \frac{\text{Abs } 1770\text{-}1700\ cm^{-1}\ (C{=}O)}{\text{Abs } 1379\ cm^{-1}\ (REF\ -CH3)}$$



PBSA

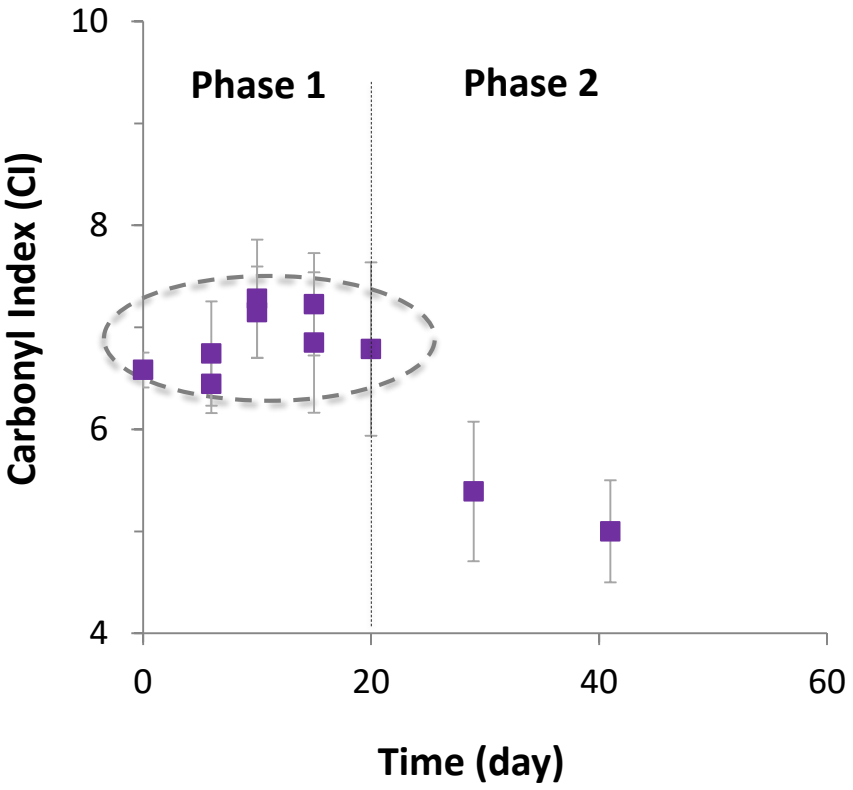
$$CI = \frac{\text{Abs } 1770\text{-}1690\ cm^{-1}\ (C{=}O)}{\text{Abs } 1473\ cm^{-1}\ (REF\ -CH)}$$



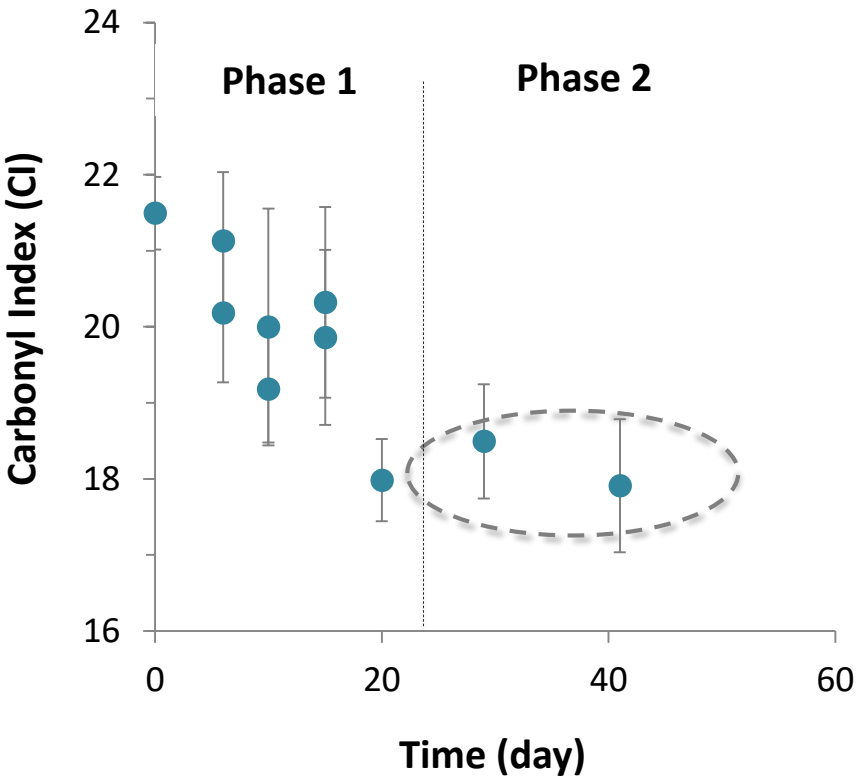
✓ Carbonyl Index => indicator of the extent of the ester linkage hydrolysis

FTIR

PHBV



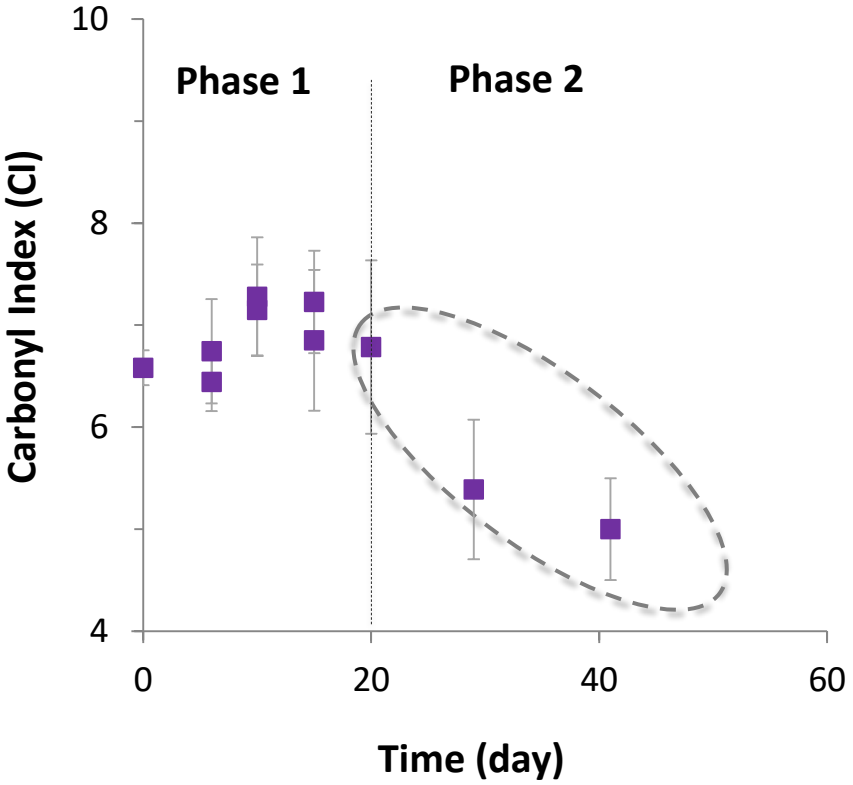
PBSA



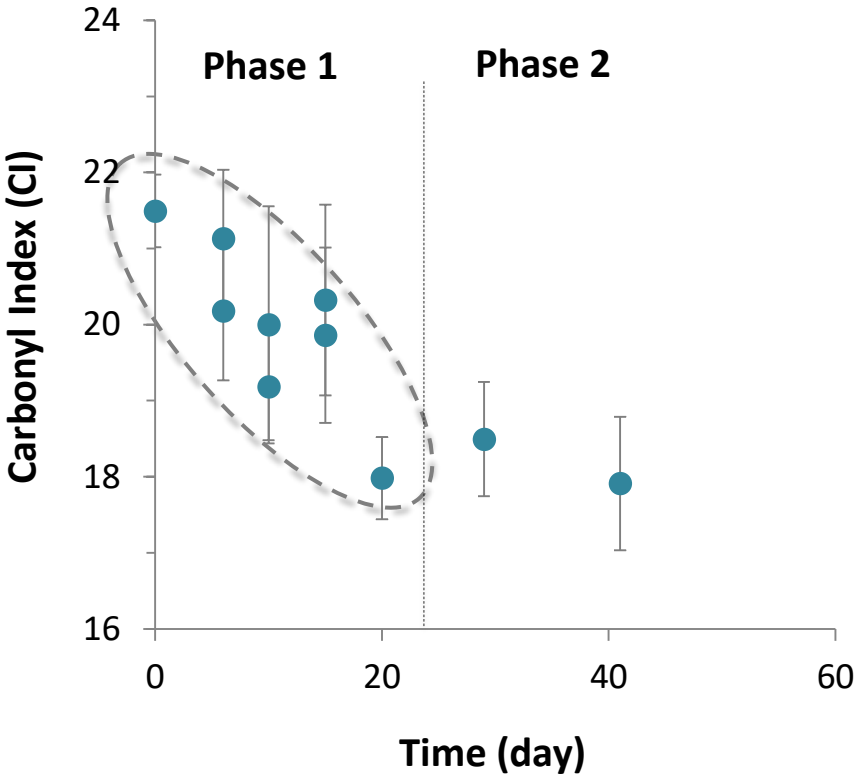
- ✓ Hydrolysis **concomitant** with erosion => no change in the carbonyl index
- ✓ Related with a **high rate** of mass loss and mineralisation

FTIR

PHBV

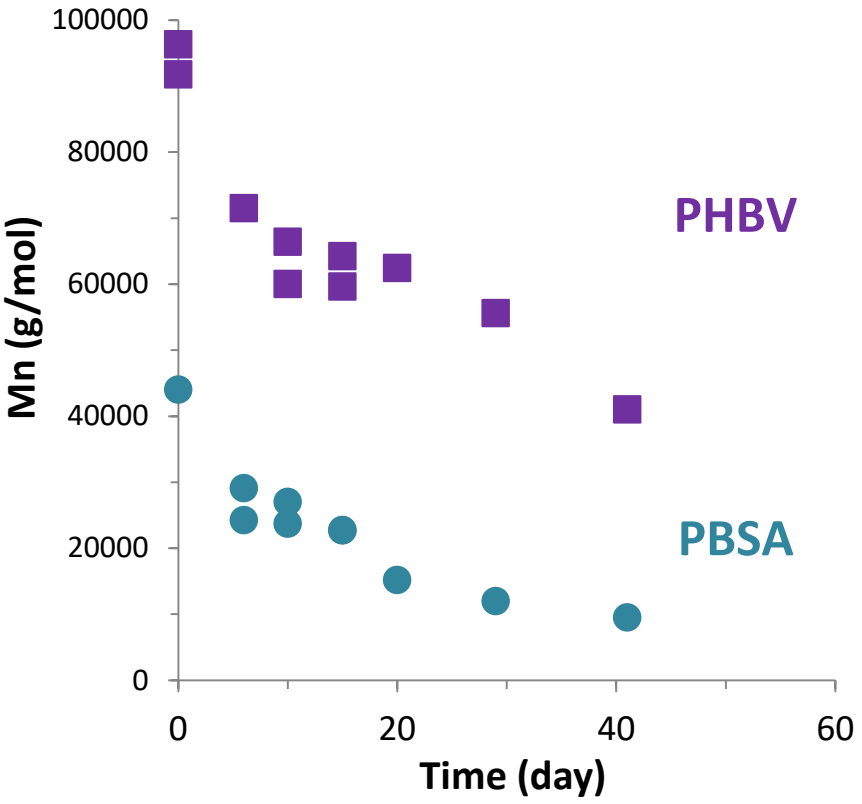


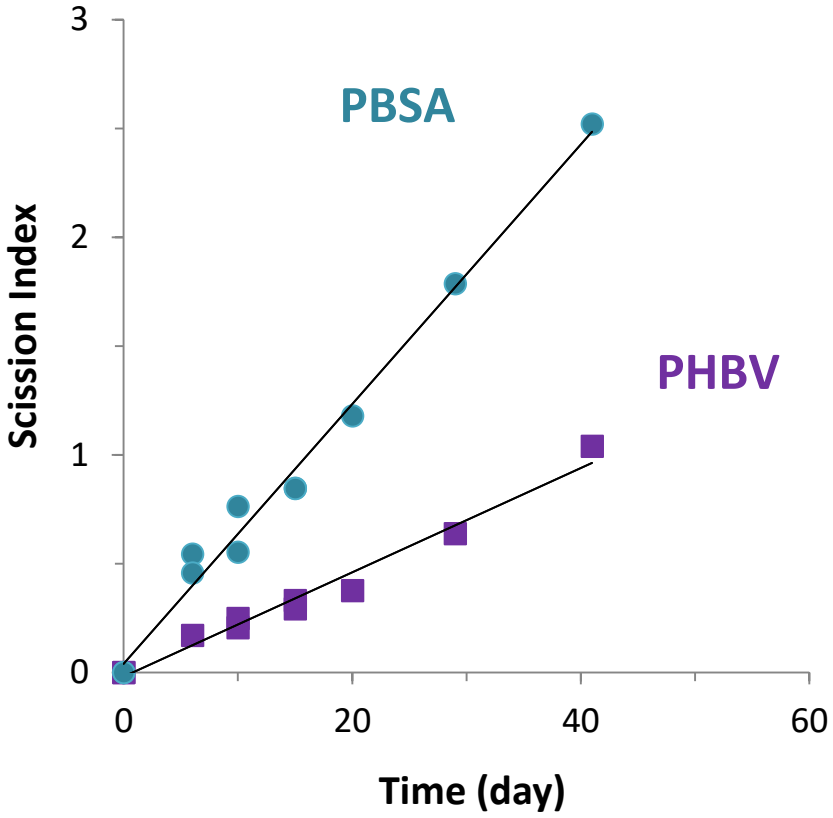
PBSA



- ✓ Hydrolysis **without** erosion/etching => decrease of the carbonyl index
- ✓ Related with a **low rate** of mass loss and mineralisation

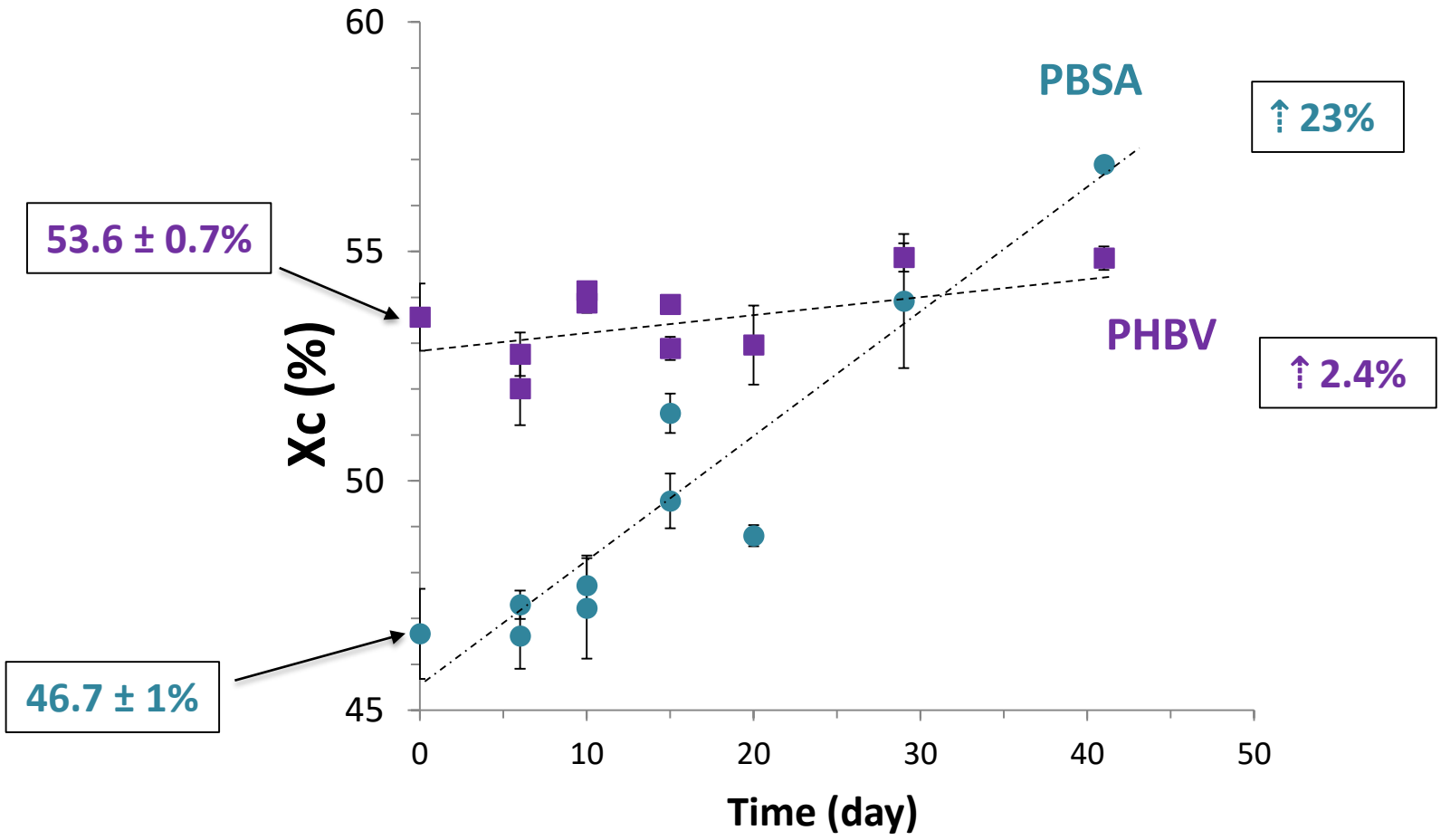
SEC





- ✓ Hydrolytic chain scission PBSA > PHBV
- ✓ Related to water permeability and diffusion => **abiotic** mechanism

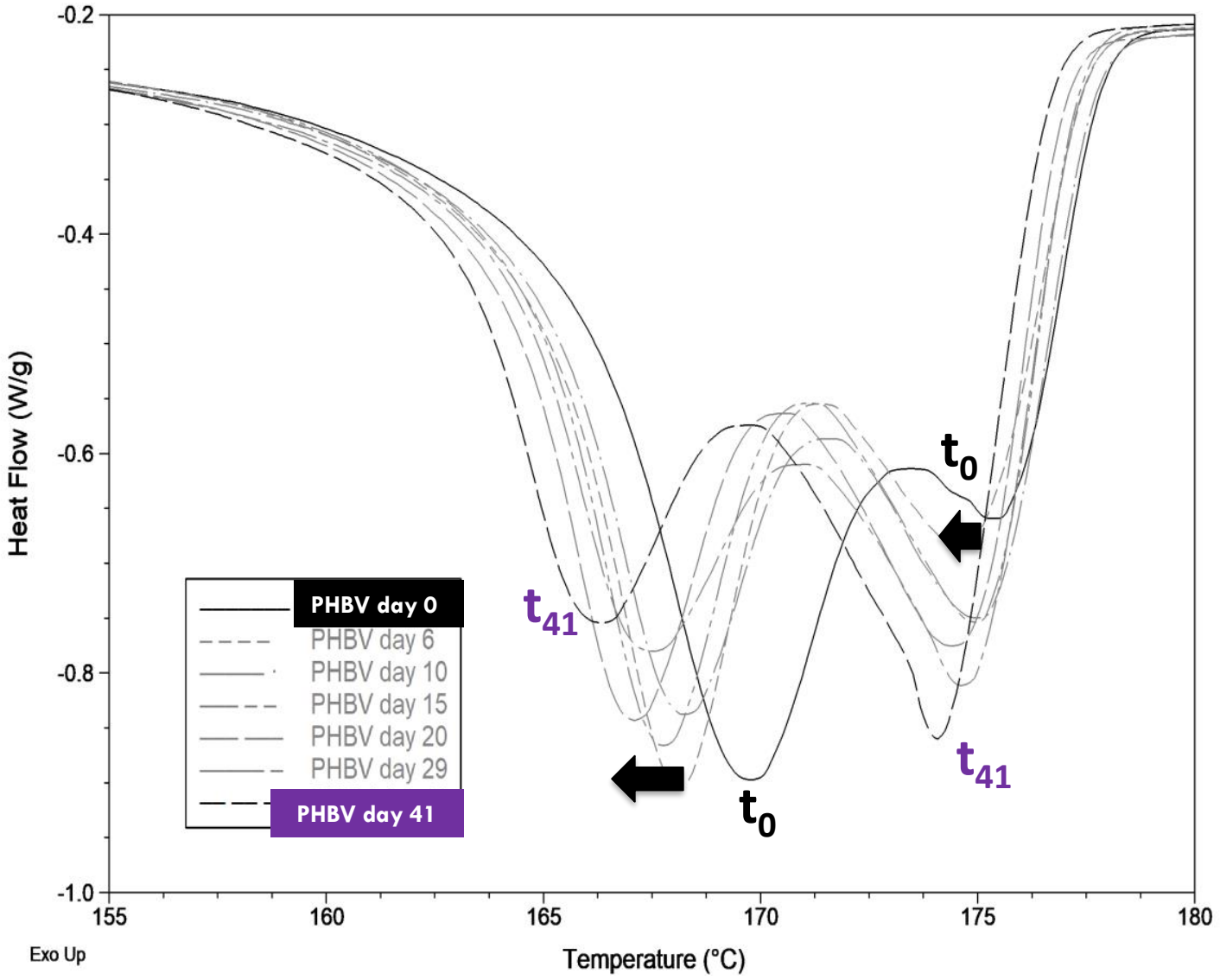
DSC



- ✓ **Hyp 1** : ≠ accessibility of the crystalline phase for micro-organisms enzymes
  PHBV >> PBSA due to ≠ morphologies and specific surface
- ✓ **Hyp 2** : recrystallisation phenomenon due to water hydrolysis of **PBSA** chains

PHBV

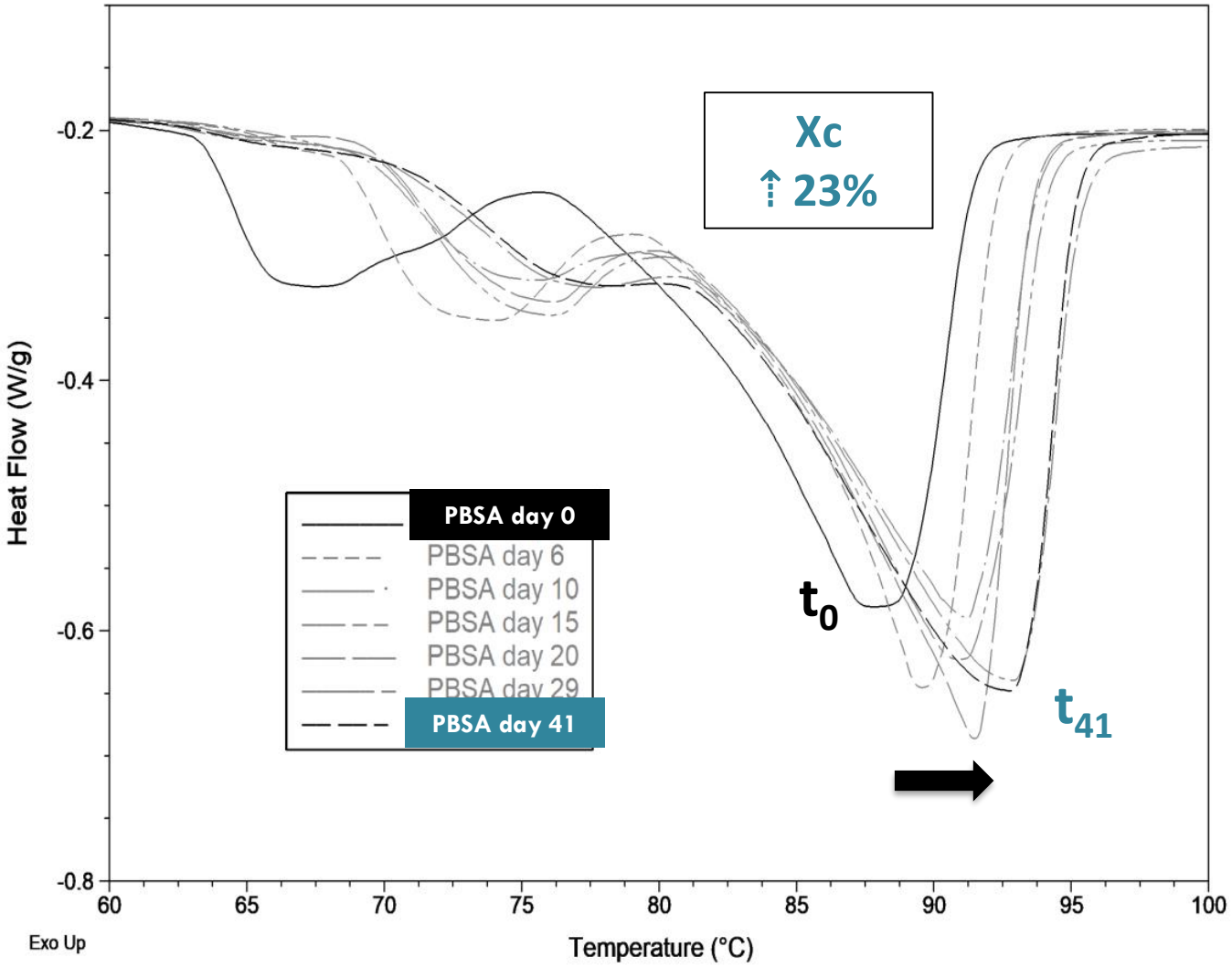
DSC

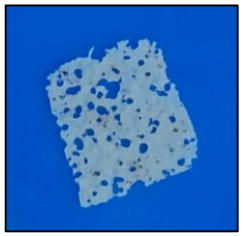


Xc
⇡ 2.4%

- ✓ new crystal populations with different morphologies and dimensions
- ✓ reduction in molecular weight of PHBV polymer chains.

PBSA





PHBV at day 20

PBSA at day 20

- ✓ **Increase in T_m** reflecting a lower flexibility of polymer chains
- ✓ **Increase of X_c** reflecting an increase in the level of structuration of the crystals
- ✓ Behaviour in link with the **ability of PBSA to fragment** during degradation in compost

PLA

Pellets
amorphous
semi-crystalline (Xc = 31%)

Packaging material
semi-crystalline Xc= 25%)

LYS VEGANBOTTLE PACKAGING
DESIGN · ENGINEERING · PRODUCTION

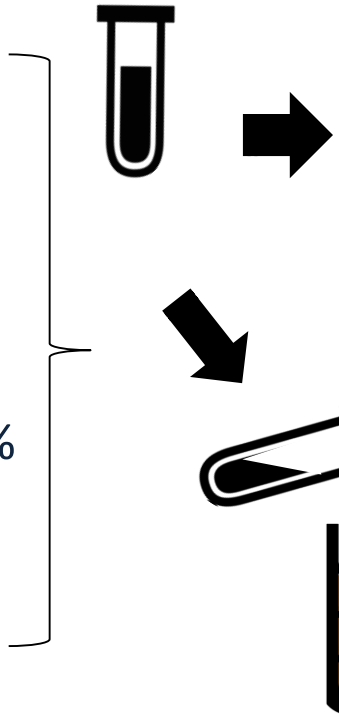
Thermo-chemical treatments

Pellets
Pieces of bottle

24 à 48h

Water / KOH 2%, 20%

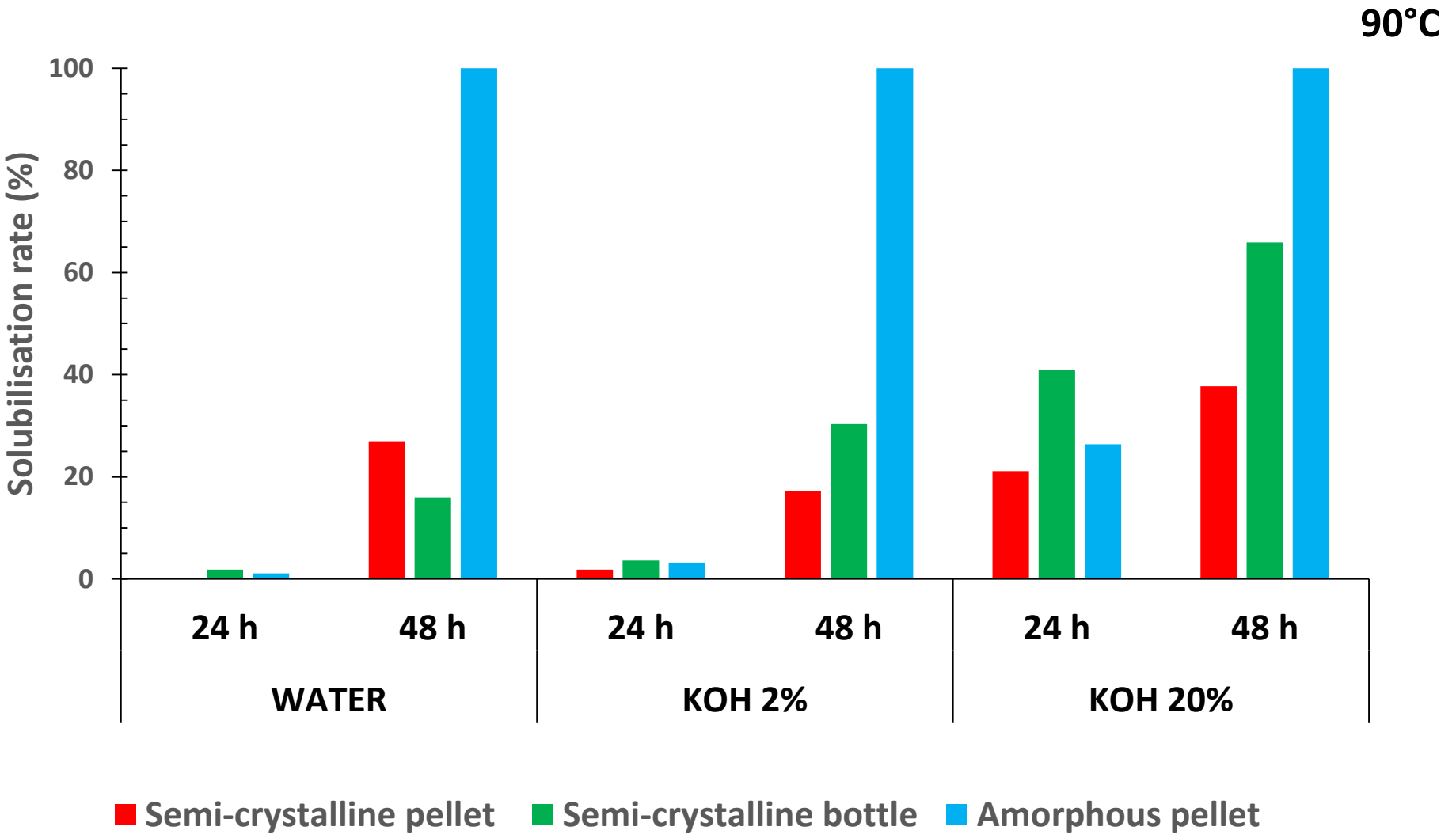
70-90-100°C



Physical-Chemical Analysis

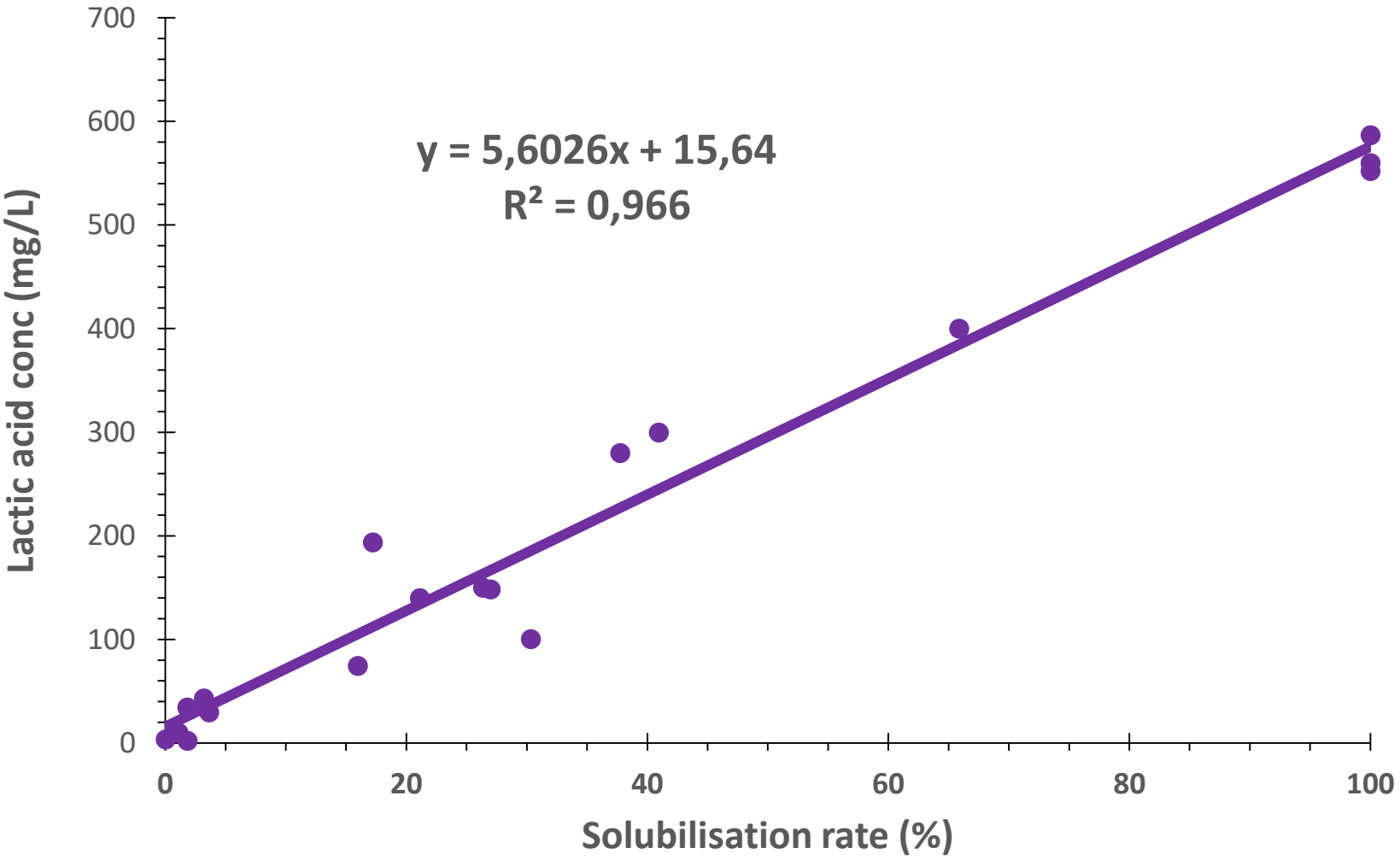
- Solubilisation rate (weighting)
- [lactic acid] (HPLC)
- Thermal stability (TGA)
- Tg, Xc (DSC)
- Biodegradation (respirometry)

Impact of thermo-chemical treatment on PLA solubilisation



- ✓ Solubilisation rate of PLA is related to polymer crystallinity
- ✓ Solubilisation rate of PLA increases with the duration of the treatment

Relation between solubilisation and hydrolysis



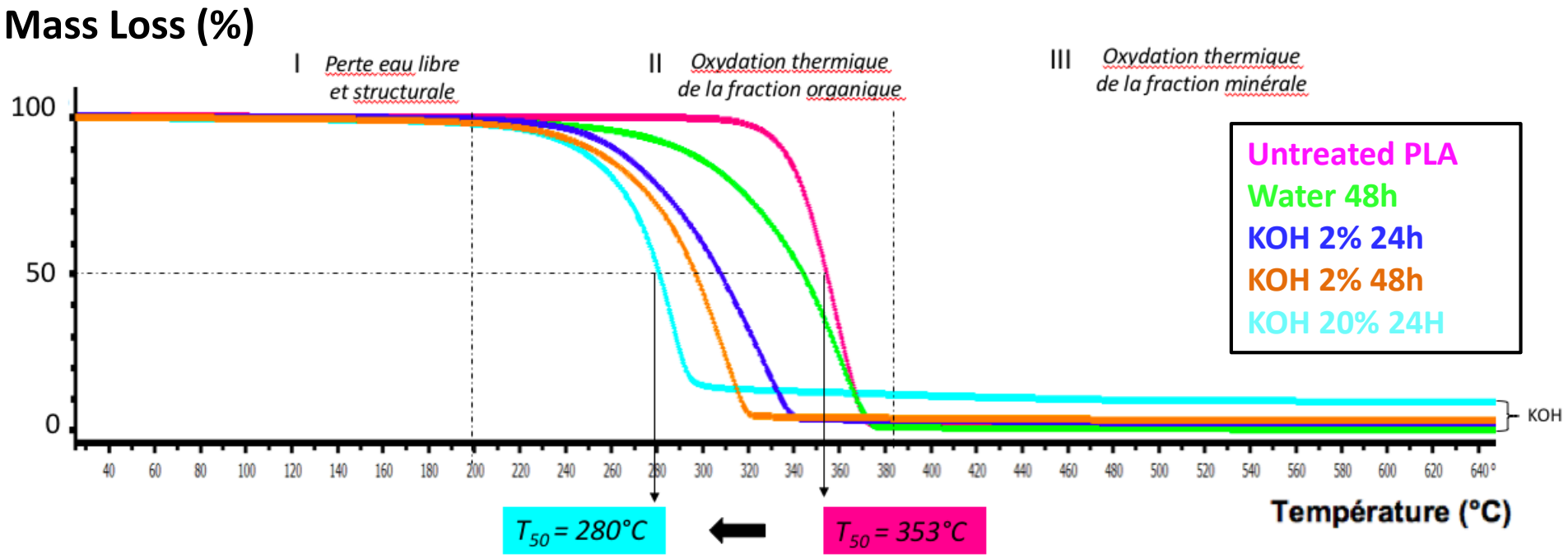
✓ Good correlation between solubilisation and hydrolysis whatever the degree of crystallinity and type of treatment

Impact of hydrolysis on thermal stability

Semi-crystalline bottle

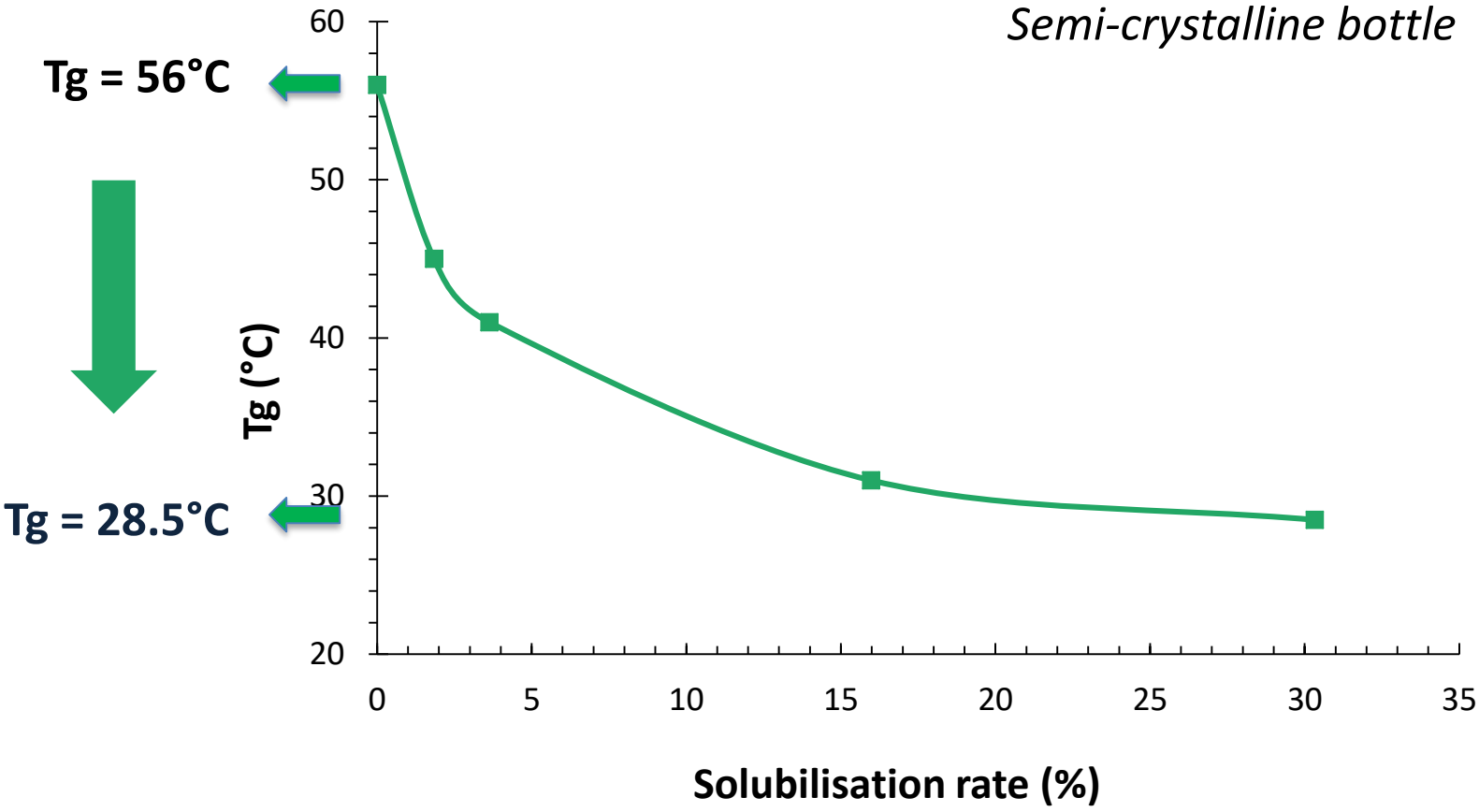
TGA

N2



✓ Solubilisation rate <=> thermal stability

Impact of PLA hydrolysis on Tg

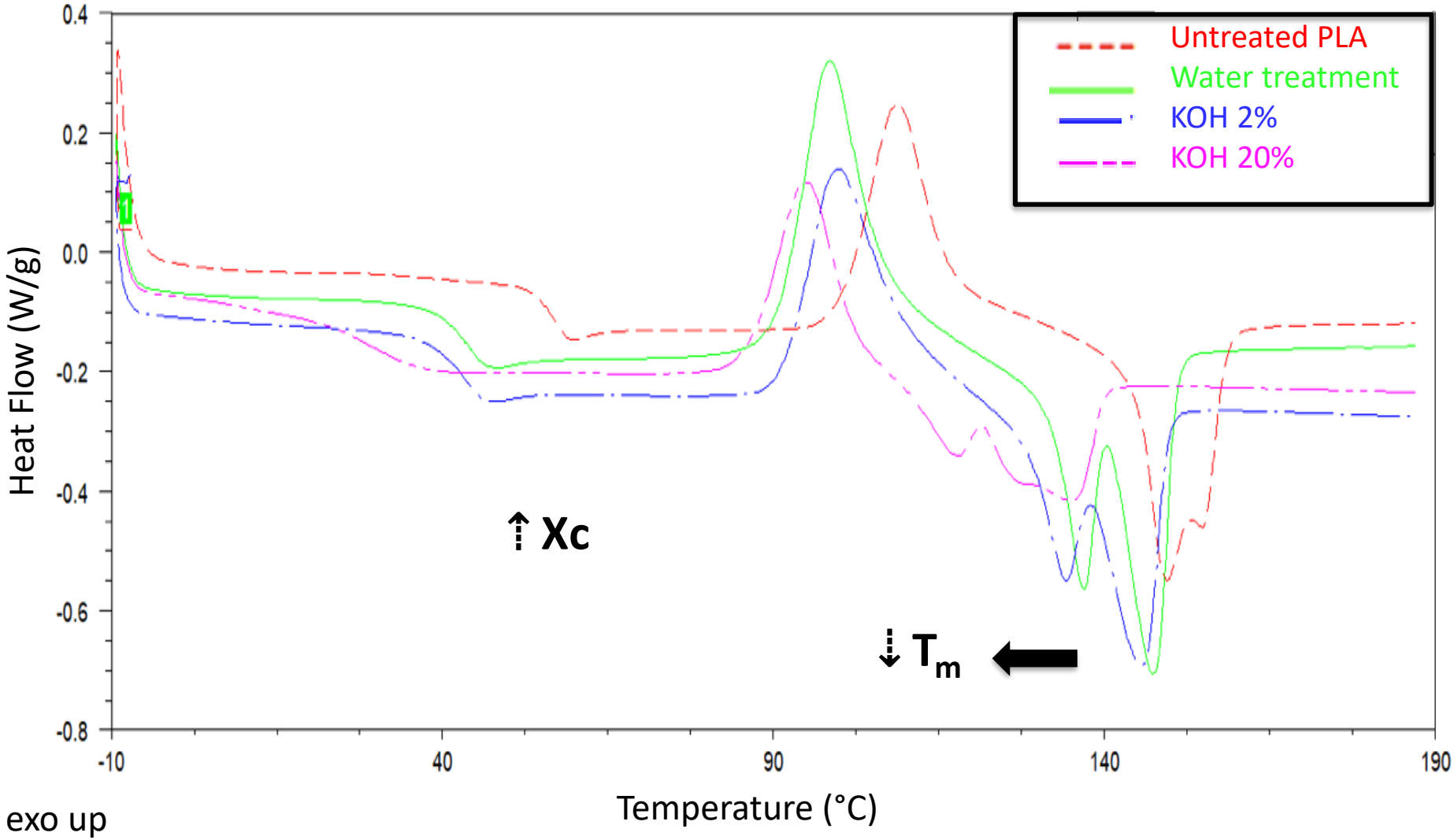


↗ Solubilisation rate <=> ↗ Hydrolysis rate <=> ↘Tg
↗ Chain mobility with decrease in Mw

Impact of hydrolysis on thermal properties

DSC

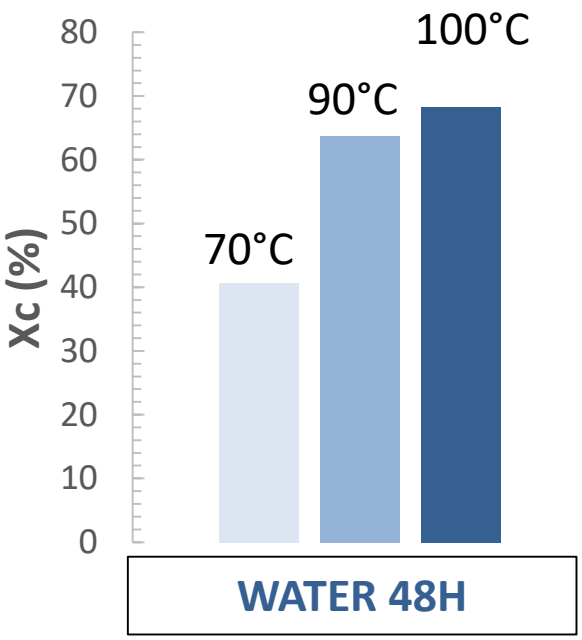
Semi-crystalline bottle

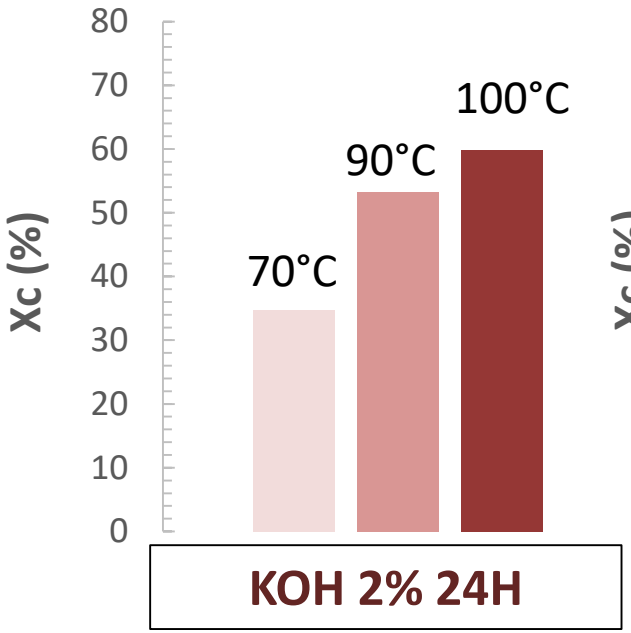


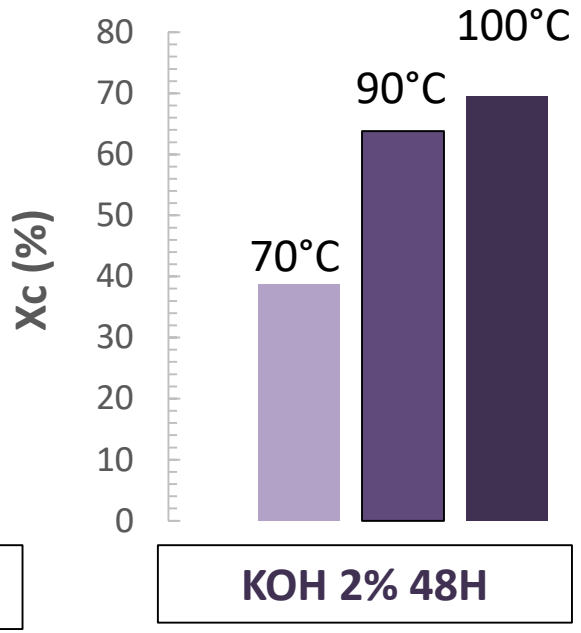
Impact of hydrolysis on crystallinity

Semi-crystalline bottle

↑ Xc





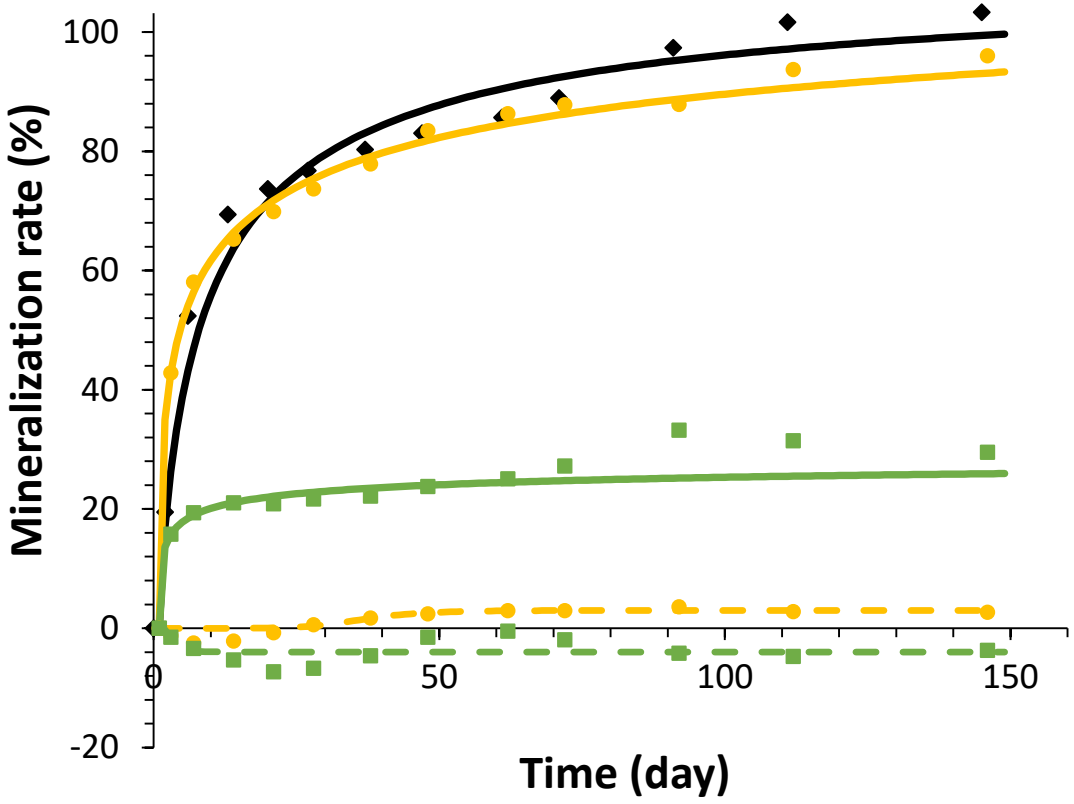


✓ ↗ Hydrolysis rate => => ↗ crystallinity rate

Impact of hydrolysis on biodegradability

Home composting conditions (28°C)

Water treatment @ 100°C



Ref = cellulose

Amorph. PLA - Water

Semi-cryst PLA - Water

Amorph. PLA untreated

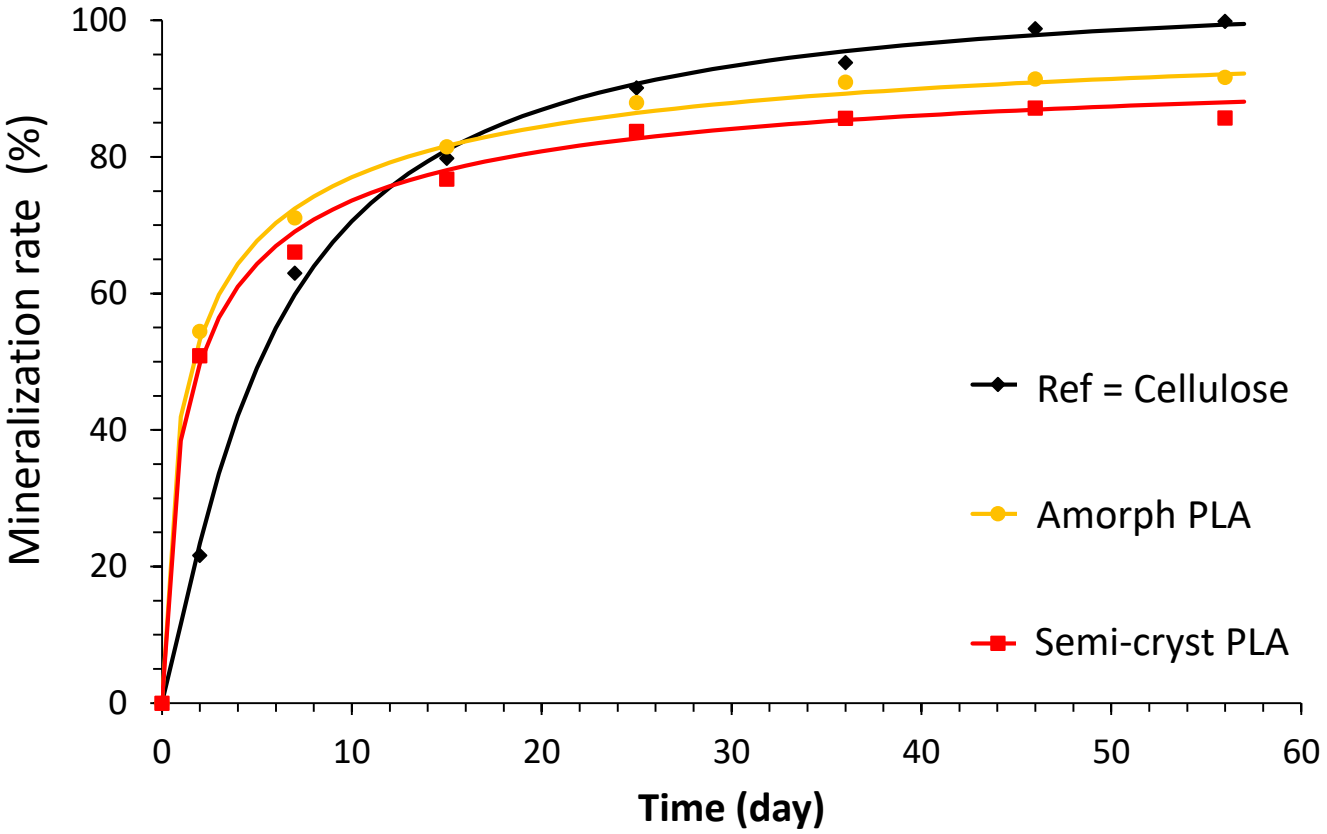
Semi-cryst PLA untreated

✓ Biodegradation in mesophilic composting conditions improved but not achieved for semicrystalline PLA after thermal water treatment

Impact of hydrolysis on crystallinity

Home composting conditions (28°C)

KOH 2% treatment @ 70°C



✓ Biodegradation in mesophilic composting conditions achieved for both amorphous and semicrystalline PLA after thermal KOH treatment

Among the different methodological approaches used to monitor the degradation status of polymer during the biodegradation process

- **the changes in thermal properties and notably the decrease in Tg and the increase in Xc appear as relevant indicators of molar mass decrease**

Perspectives

- **Study the end-of-life performance of biodegradable plastics and packaging through the existing organic valorization routes**
- **Improve the biodegradability of PLA and PBAT in mesophilic conditions**
- **Provide data demonstrating the non-persistence of residual compostable micro-fragments**

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