PHA
We all know (and literature repeats this since 1988)

- PHB has properties like PP, but becomes brittle with time
- PHB degrades at melting temperatures
- PHB melt is too liquid to decently mold
- PHB ……..

1988 first paper on properties

If you try to convince a plastics processor using PHA and have to cite these properties, then he answers:

This polymer is from renewable resource. Good.
But far away from our needs.
My customer needs reliable and perfoming thermoplasts.
Bio is not enough.

So the question arises:

How can you transform the biopolymer into a bioplast?

My suggestion: Imagine what the molecule tells you, then act

(Let me analyze each point)

- PHB has properties like PP, but becomes brittle with time
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1) PHB has properties like PP, but becomes brittle with time

Imagine what the molecule tells you:

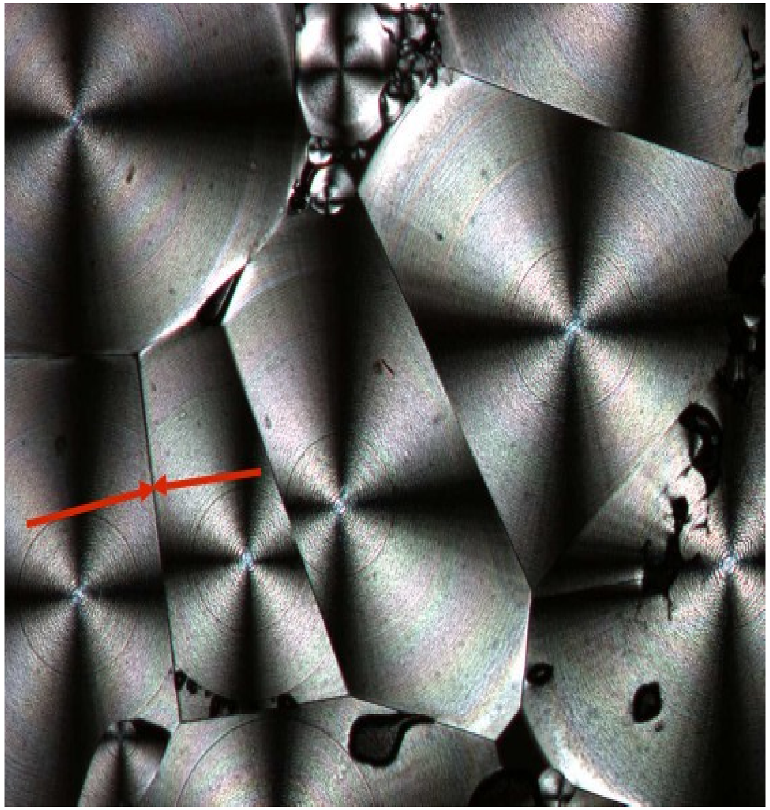
- **it is absolutely linear**
- **it is absolutely stereoisomer (isotactic)**
- **it is absolutely C4-C4- repetition units**

Consequence every chemist will tell you: it has to crystallize! But as the molecular weight is ~1 million Dalton or more: the **speed is slow**

What then are the consequences of crystallizing PHB?

Density changes from low to high. This results in voids
→ brittle

months to reach the thermodynamic equilibrium
→ properties changes



Solutions:

- nucleate so that the travel time for the molecules is reduced to minutes
- fill the gaps

What are the consequences of crystallizing PHBV?

The sames as with PHB

But:

The extra substituent does not fit the crystal structure and thus moves to the turns of the crystal lamellae.
Expect up to 600 days at room temperature!

(means: useful for short shelf live objects, not for lasting ones)

HOSHINA *et al.*: TERAHERTZ SPECTROSCOPY IN POLYMER RESEARCH

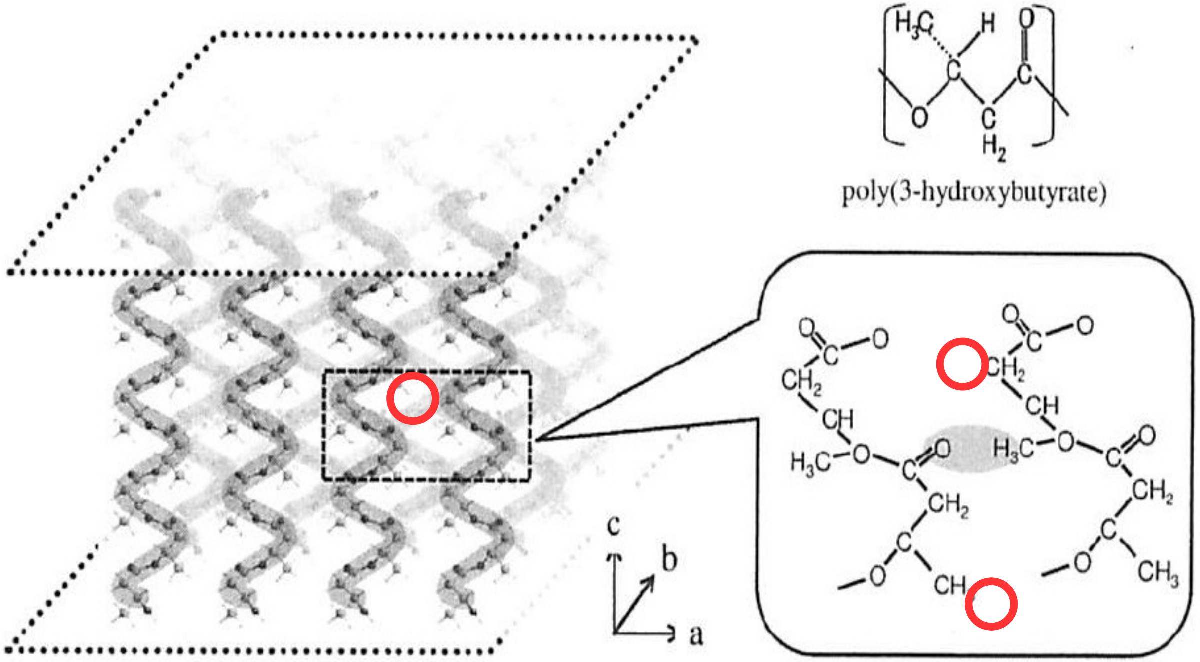


Fig. 1. Chemical structure of PHB and schematic of molecular structure of lamellar crystal.

2) PHB has properties like PP but degrades at melting temperatures

Imagine what the molecule tells you:

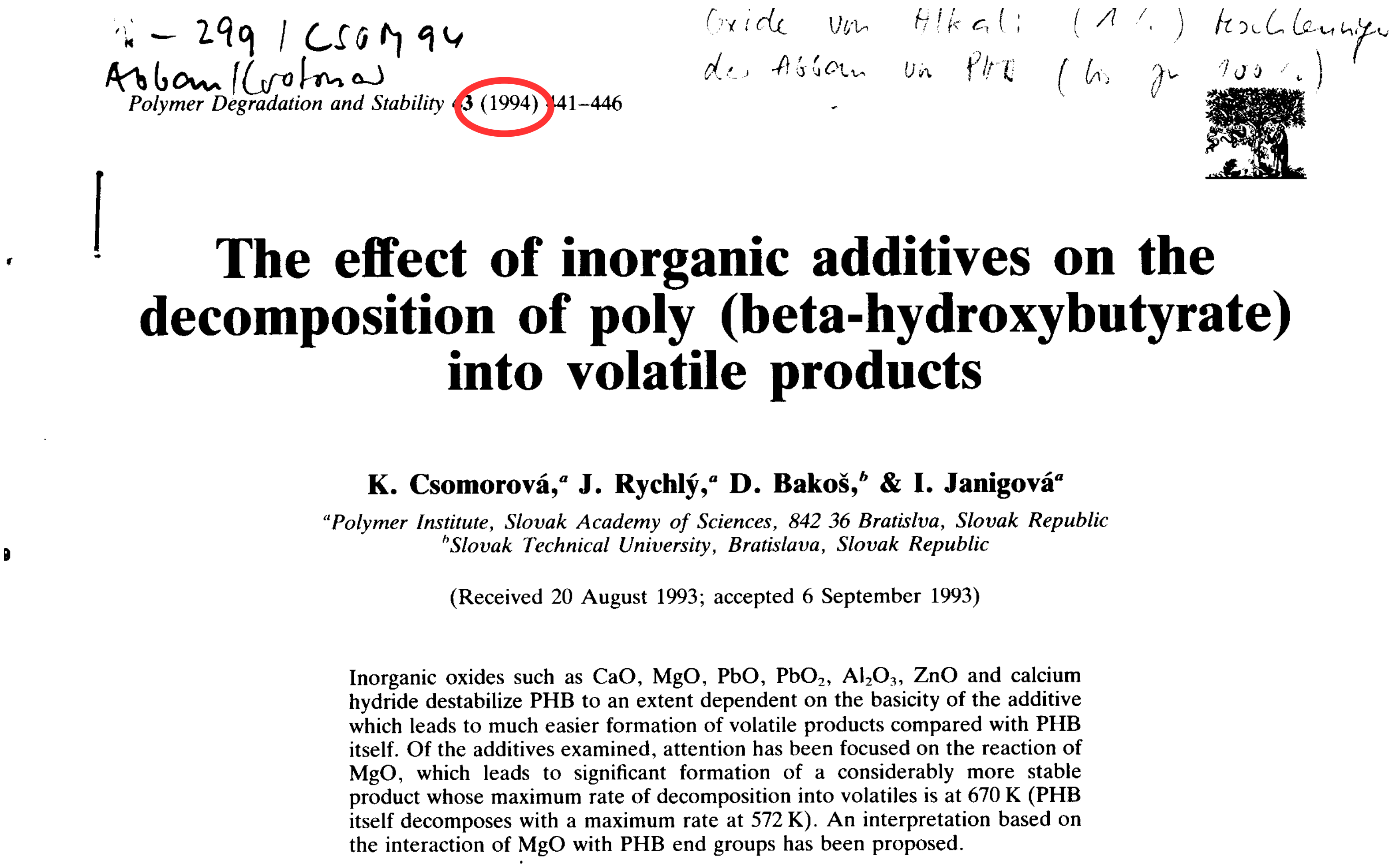
PHA are beta esters that always form a 6-ring between the the carbonyl oxygen and the activated hydrogen at the beta carbon

these 6-rings always split (even at room temperature)

and

the splitting is catalyzed by earth alkali ions (known since 1994!)

BIOMER
biodegradable polymers
from the earth - into the earth



?i – 299 / CSOM 94
Abbau/Crotonat

Oxide von Alkali (1 %) beschleunigen
den Abbau von PHB (bis zu 100 %)

Polymer Degradation and Stability 43 (1994) 441–446

The effect of inorganic additives on the decomposition of poly (beta-hydroxybutyrate) into volatile products

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Inorganic oxides such as CaO, MgO, PbO, PbO_2, Al_2O_3, ZnO and calcium hydride destabilize PHB to an extent dependent on the basicity of the additive which leads to much easier formation of volatile products compared with PHB itself. Of the additives examined, attention has been focused on the reaction of MgO, which leads to significant formation of a considerably more stable product whose maximum rate of decomposition into volatiles is at 670 K (PHB itself decomposes with a maximum rate at 572 K). An interpretation based on the interaction of MgO with PHB end groups has been proposed.

Kim et al. Polymer Degradation and Stability **91** (2006) 769-777

Solutions:

- avoid or complex Ca^{++} and Mg^{++} during extraction
- use deionized water in cooling water bath in compounding

3) PHB has properties like PP but melt is too liquid to decently mold

Imagine what the molecule tells you:

PHA have no branches whatsoever
→ molecules behave like hot spaghetti in boiling water

Solution: **melt, then rapidly cool (as with spaghetti):**

(use negative temperatures in processing)

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(use negative temperatures in processing)

Let me summarize

- PHB has properties like PP, but becomes brittle with time
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Applying all the insights given above, did we do OK at Biomer?

Feedback from users:

- no problems with molding
- cycle times as good or even better than with PP
- parts don't change properties over years
- parts bear loads better than polyolefines
- parts are more UV resistant than polyolefines

- fringe benefit: from renewable resources, biodegrade

(I would say that our PHB based resins perform)

I hope that I was able to point to the factors on how to transform the biopolyester into a bioplast

Thank you for being interested in a most interesting thermoplast!

(I mean: one of the most interesting thermoplasts!)

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