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Session: Processing
Presentation by: Jürgen de Jong, *Synbra Technology bv*

Title: **Extrusion foaming process for polylactic acid (PLA)**

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Curriculum:
Mr. Jürgen de Jong graduated as a polymer chemist in 1998 at Eindhoven University of Technology. He did his final research in the group of Prof Lemstra in the field of reactive processing of polyetherimide (PEI).
After his graduation Jürgen joined Stahl Holland and later Stahl International in Waalwijk, The Netherlands. He did extensive research on polyurethane (PU) coatings for flexible substrates. In the last year at Stahl he became responsible for scale up of new products from the lab to the factory as head of the pilot plant.
Since 2007 Jürgen is working for Synbra Technology in Etten-Leur, The Netherlands. He started as Senior Product Developer leading various projects concerning new types of expandable polystyrene (EPS). Soon the development of BioFoam® became his main task. BioFoam® is a polylactic acid (PLA) based foam having properties comparable with EPS. Besides studying the best way to foam PLA, Jürgen has also cooperated in the development of a new PLA polymerization process and the erection of PLA polymerization plant at Synbra's site in Etten-Leur. The latter has been done together with Total-Corbion, The Netherlands, and Sulzer ChemTech, Switzerland.
In 2017 Jürgen became the R&D manager for Synbra Technology. In this role he is still responsible for the development of BioFoam® and PLA (Synterra®). Next to this Jürgen is also involved in the field of EPS, EPP and Xire, Synbra's new incombustible EPS.

Abstract:
Synbra Technology is the raw material supplier and in-house innovation center of the Synbra group that comprises also EPS foaming and molding companies like IsoBouw and Synprodo. Just recently the Synbra group has been bought by the Swedish BEWi group and merged into BEWi-Synbra. The new company will still have its innovation center in Etten-Leur and is eager to roll out BioFoam in Europe. BioFoam® is a way to secure BEWi-Synbra's leading position in EPS and extend 50 years of polymer foaming.

At the moment BioFoam® parts are leaving the factory to go into packaging and construction applications. Examples are fish boxes and particles for cavity-fill. Use of BioFoam® in other applications is considered as well. Comparing the properties of BioFoam® and conventional EPS a remarkable resemblance is found, but with the added value of being based on renewable feedstock and having a lower carbon footprint. This is also expressed by the Silver Cradle-to-Cradle certificate.

To facilitate further expansion of BioFoam the production process has to be more efficient. One way to simplify the bead foaming process is to consider extrusion foaming. This would

eliminate CO2 impregnation of microbeads and would introduce melt foaming instead of solid state foaming. As extrusion is already used to make microbeads it makes sense to do the foaming in this step as well.

In the presentation BEWi-Synbra is presented and the production of BioFoam is explained. Afterwards the advantages and points of attention of extrusion foaming are shown, which is then followed by introduction of the FOAMEX project and its partners. Some of the work performed in the FOAMEX project is presented, especially the work conducted at BEWi-Synbra. This considered large scale production of a new branched PDLA polymer to be used with ordinary PLA. The unique branched structure should improve melt strength during foaming which should result in better control of the foaming process and better foams. The results of various rheological measurements will be shown to prove the different structure of the new PDLA type.

Extrusion foaming process for polylactic acid

Jürgen de Jong

BEWi-Synbra

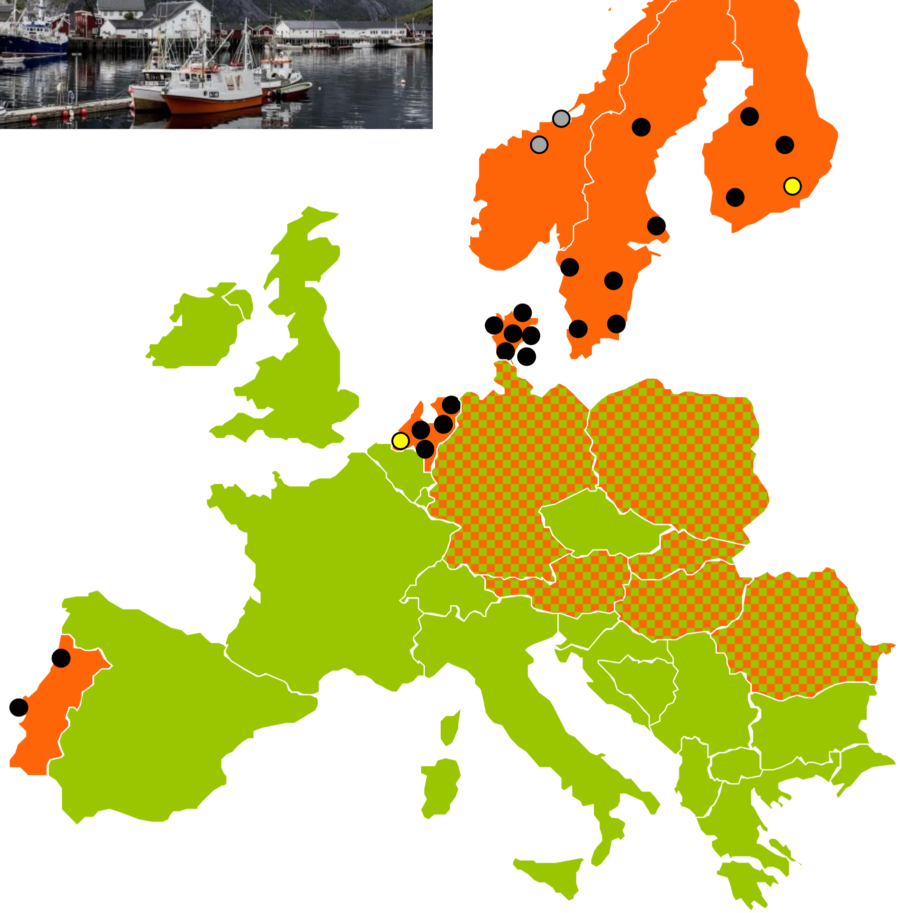
Synbra

Company introduction

BEWi Synbra GROUP

- Dutch holding of 13 companies;
- Synbra Technology supplies Expandable PolyStyrene (EPS);
- E.g. Isobouw, Synprodo convert EPS beads into foamed pearls and products;
- Focus on Sustainable Insulation Systems (SIS) and Industrial Products & Solutions (IPS);
- Synbra Technology is also center of Innovation.

Company introduction



BEWi Synbra GROUP

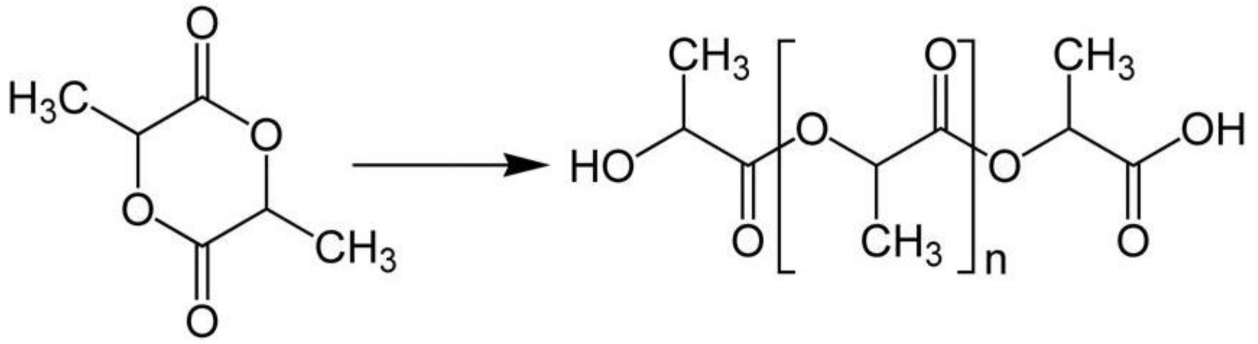
- One company;
- Two sites for EPS raw material production (upstream);
- 22 sites for EPS foaming and molding (downstream);
- Strategic collaboration in eastern Europe (Hirsch Porozell).

PLA project

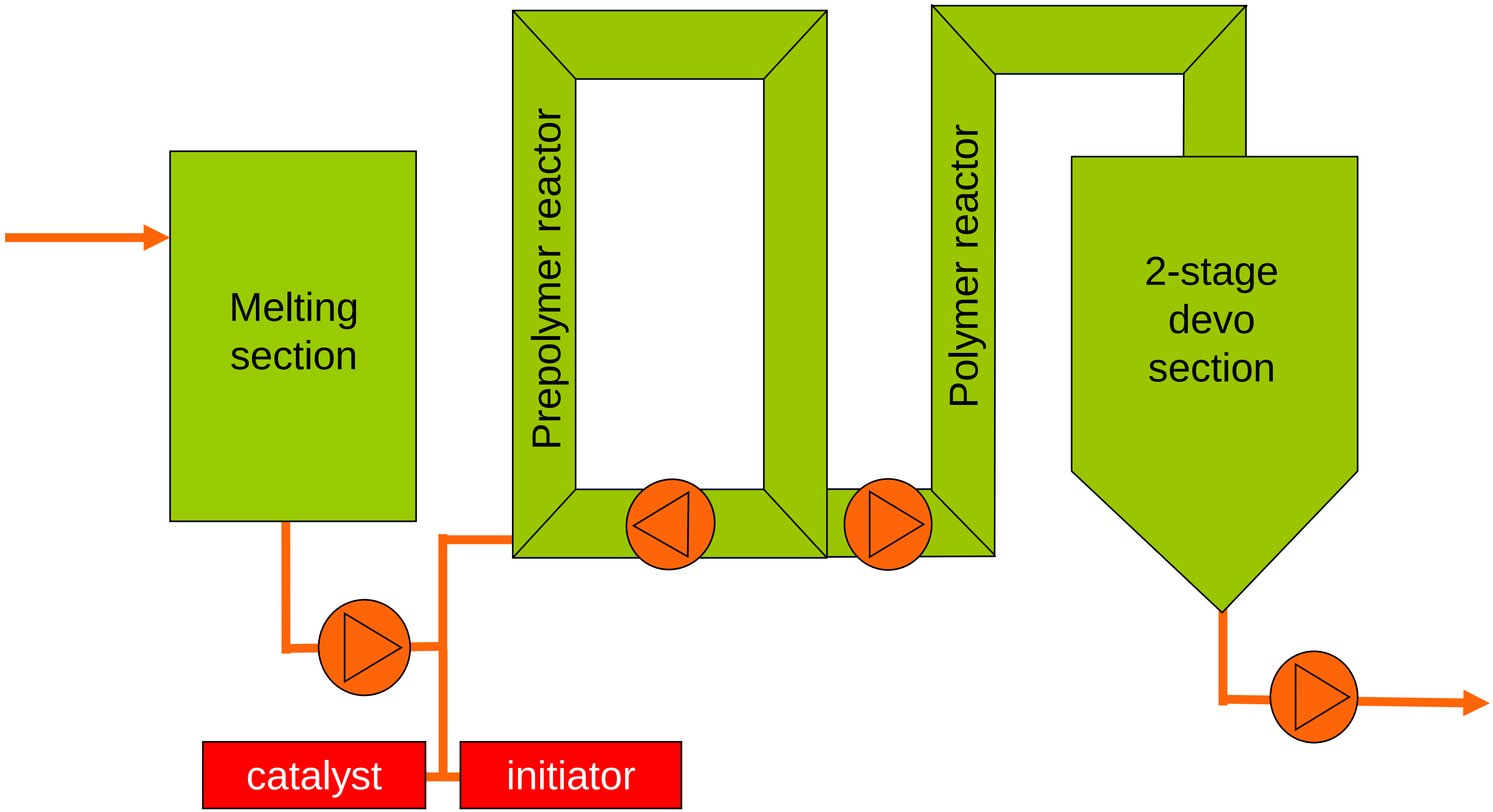
- Formal project started in April 2006;
- R&D with Wageningen University & Research;
- Use EPS expansion & moulding technology;
- Use Poly(Lactic Acid) & CO_2;
- Improved shape molding with special adhesive;
- Patents: WO2008130225 & WO2008130226;
- Integrated raw material supply (PLA polymerization);
- Trade marks BioFoam® & Synterra®.

PLA polymerization

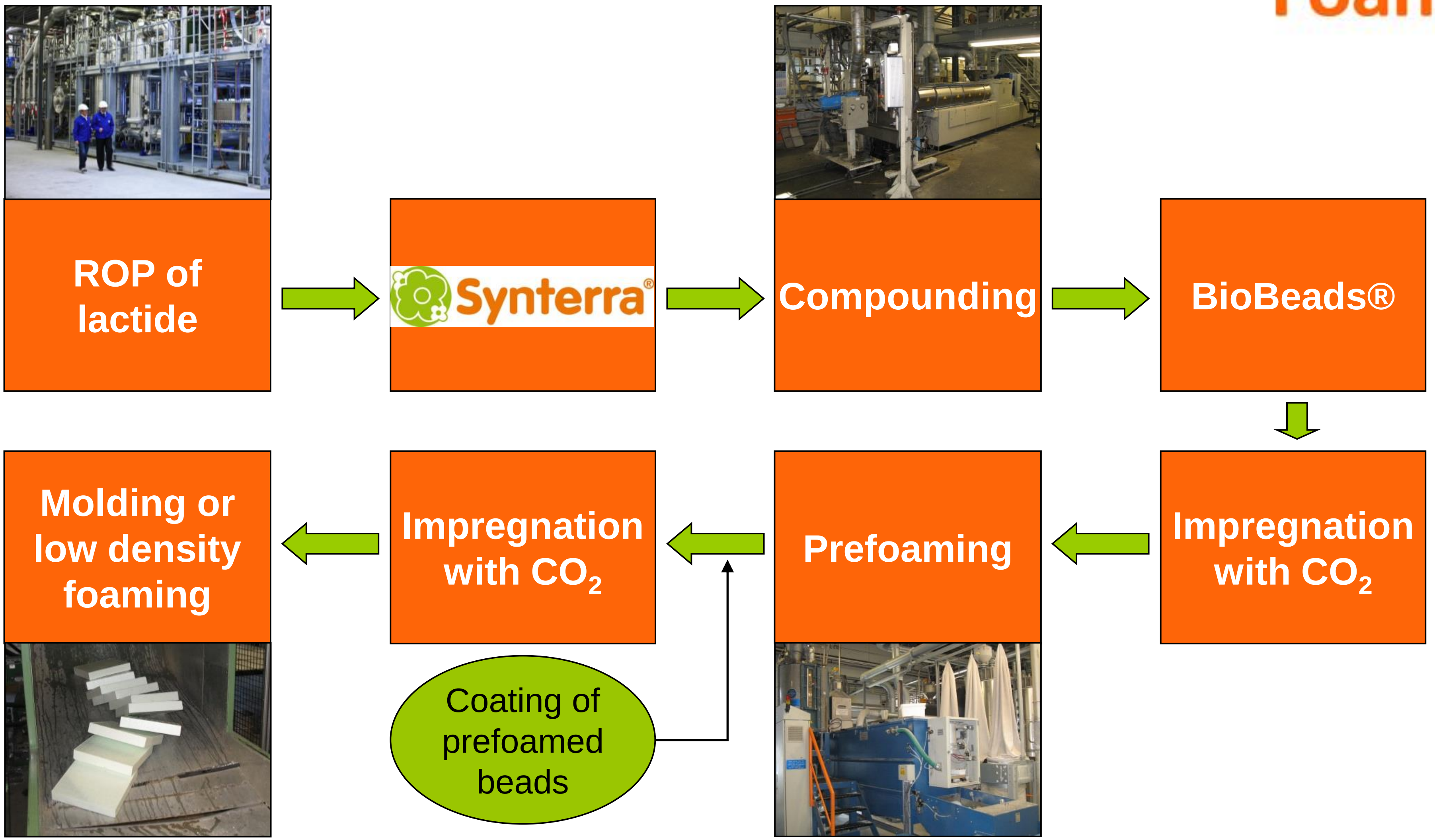
- Starting point is lactide;
- Polymerization of lactide requires:
  1) Temperature (160 - 220°C);
  2) Residence time (depends on temperature);
  3) Special additives (catalyst, initiator, stabilizers):
     - Catalyst (to speed up reaction);
     - Initiator (to control molecular weight);
     - Stabilizers (to prevent degradation).



PLA polymerization

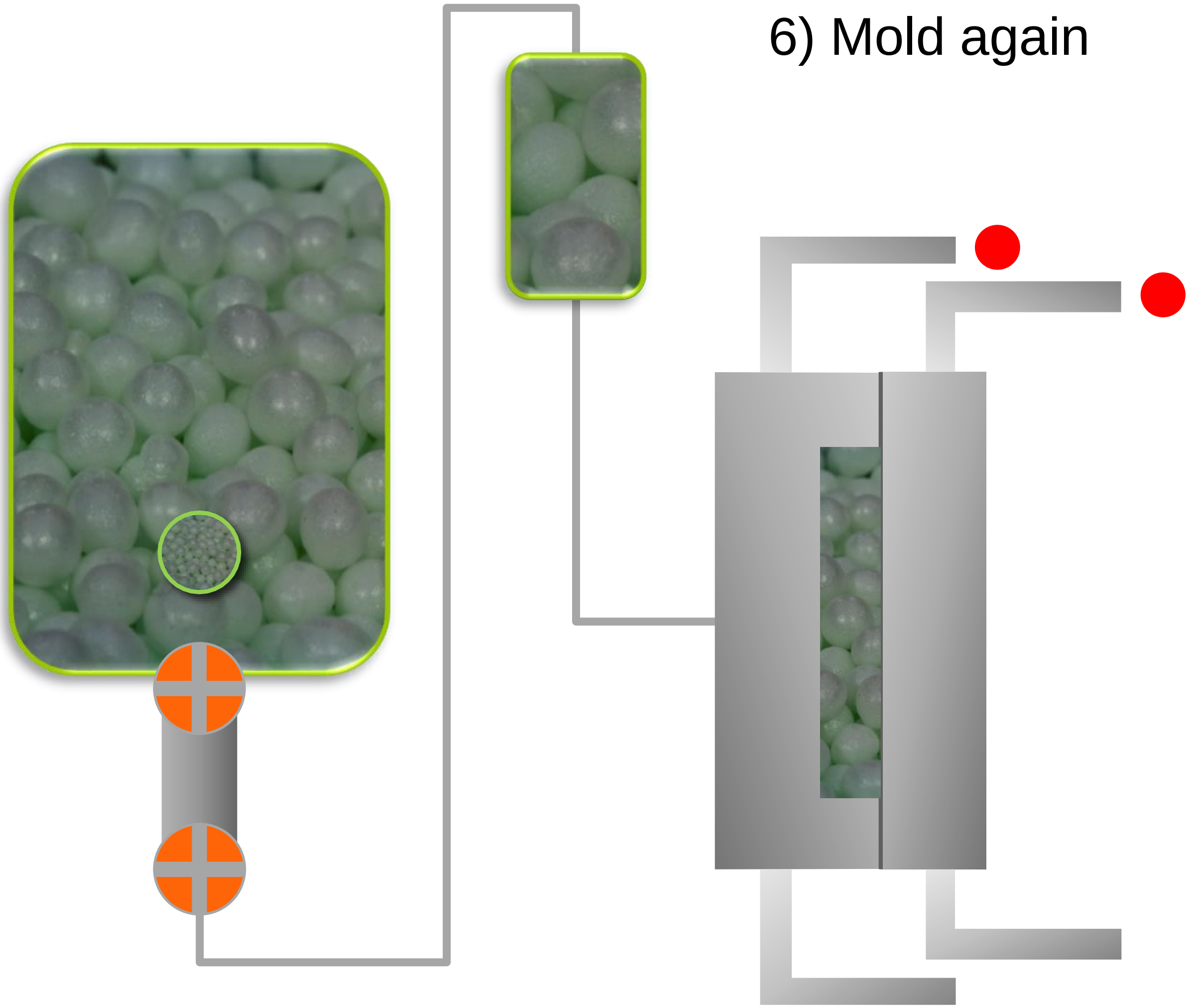


BioFoam® process



BioFoam® process

6) Mold again



BioFoam® process

ROP of lactide

Synterra®

Compounding

BioBeads®

Impregnation with CO_2

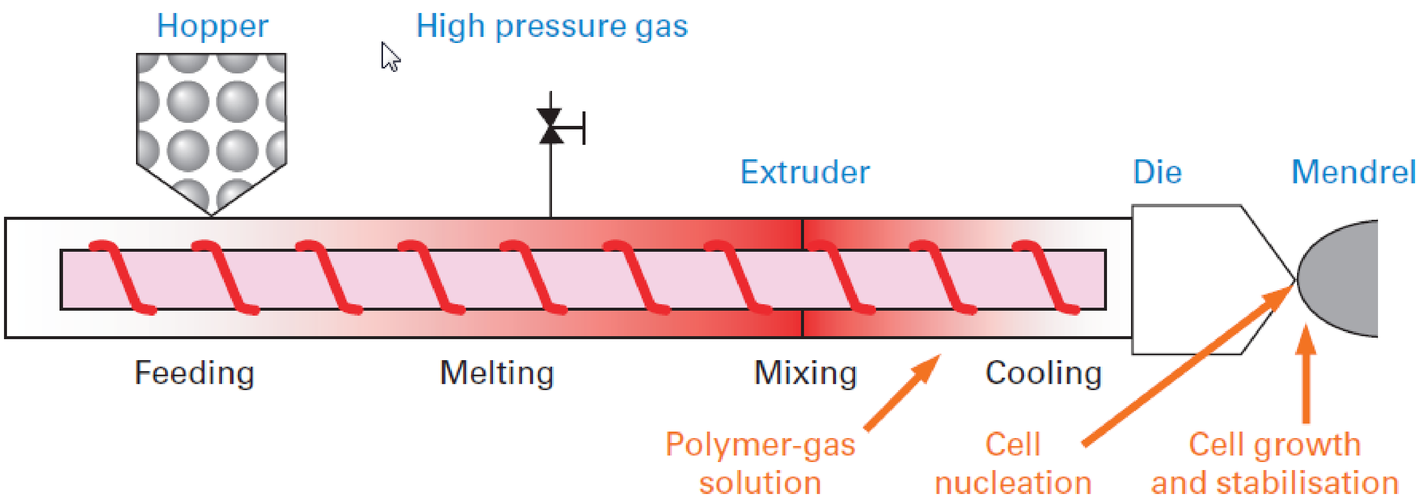
Prefoaming

Coating of prefoamed beads

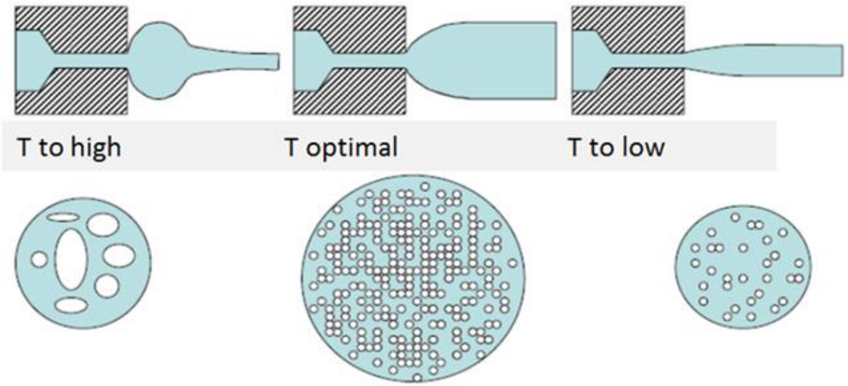
Impregnation with CO_2

Molding or low density foaming

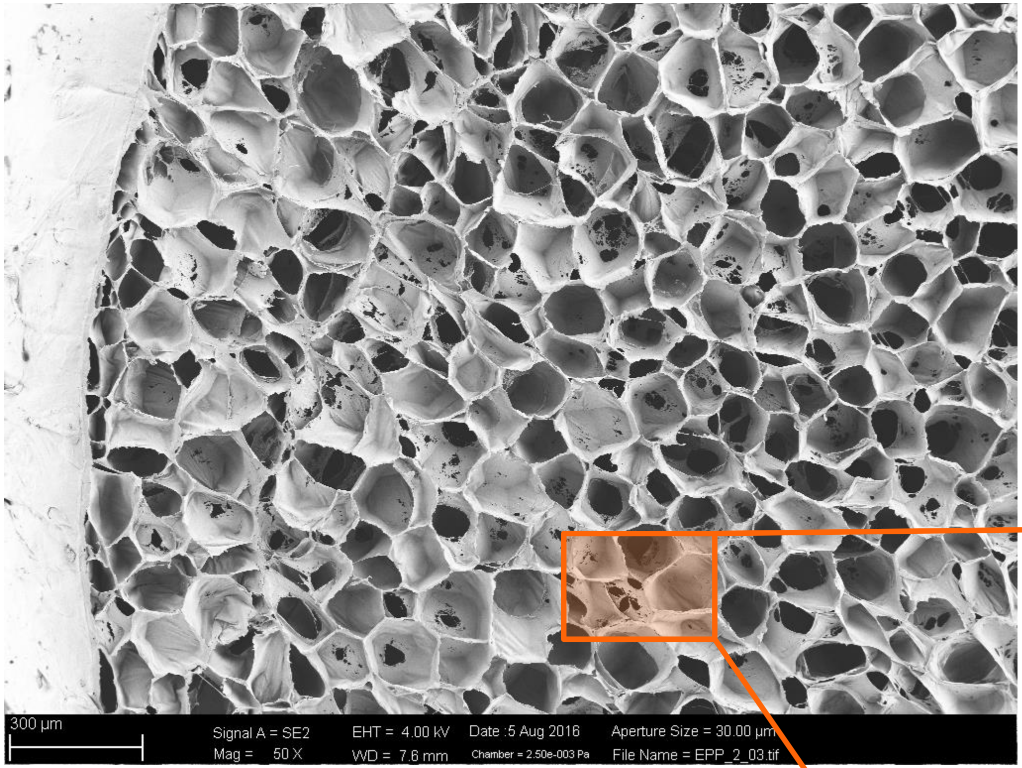
Extrusion foaming

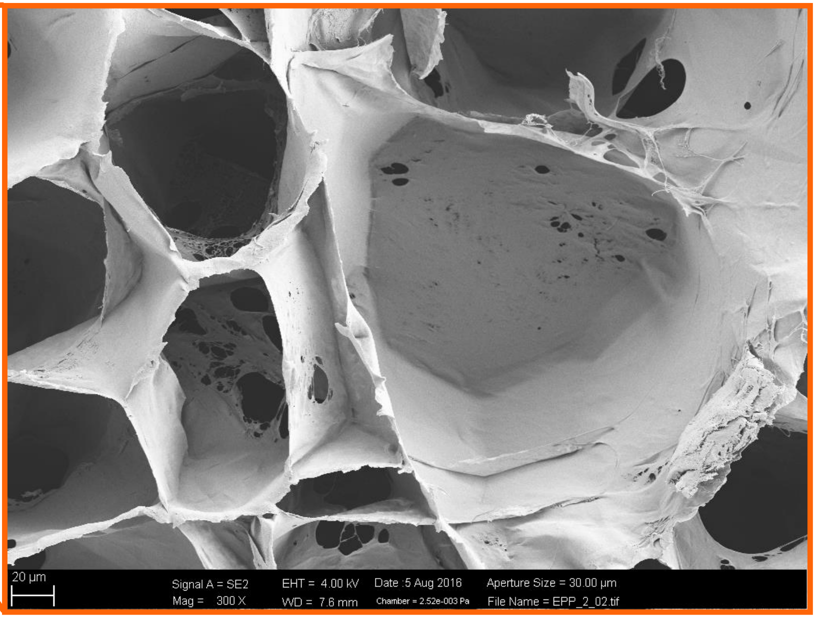


- Elimination of first step in BioFoam process;
- Melt foaming ↔ solid state foaming;
- Melt strength by cooling or polymer structure.



Extrusion foaming





FOAMEX

Goal:

Development of a reproducible and stable extrusion foaming process for PLA:

- Cell size in the micron domain;
- Density and crystallinity to be varied.

Period:

- September 1st 2015 – June 30th 2018.

Possible outcome:

- Wine closures;
- Expanded beads;
- Foamed sheet.

Synbra

FOAMEX

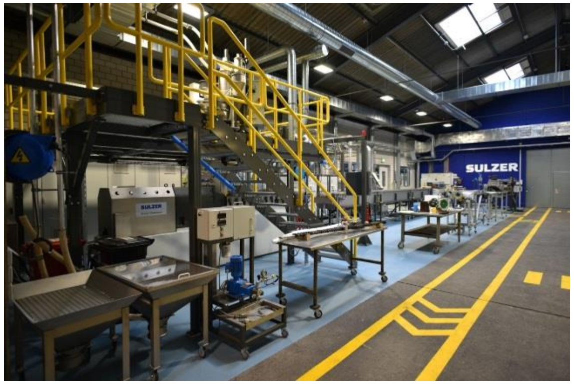
BioFoam

VINVENTIONS

- Producer of artificial wine corc (foamed (bio)PE);
- Biobased wine corcs (foamed PLA);
- Small scale foaming tests.

SULZER

- Poly-ester production facilities;
- Extrusion foaming equipment;
- Small scale foaming tests;
- Caracterization of polymers.



FOAMEX

WAGENINGEN
UNIVERSITY & RESEARCH

- Small scale polymerisation;
- Characterisation of materials;
- Characterisation of products.

BEWI
Synbra
GROUP

- PLA polymerization;
- BioFoam® products;
- Molding trials.

FOAMEX

Goal:

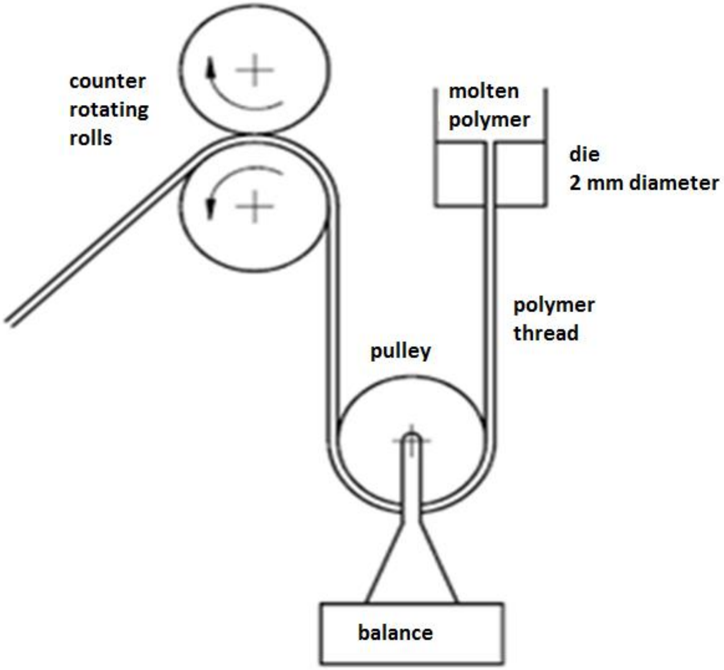
Development of a reproducible and stable extrusion foaming process for PLA.

Challenge:

Foam properties are governed by interaction of material properties and equipment.

Melt strength:

Extensional viscosity is the resistance to stretching



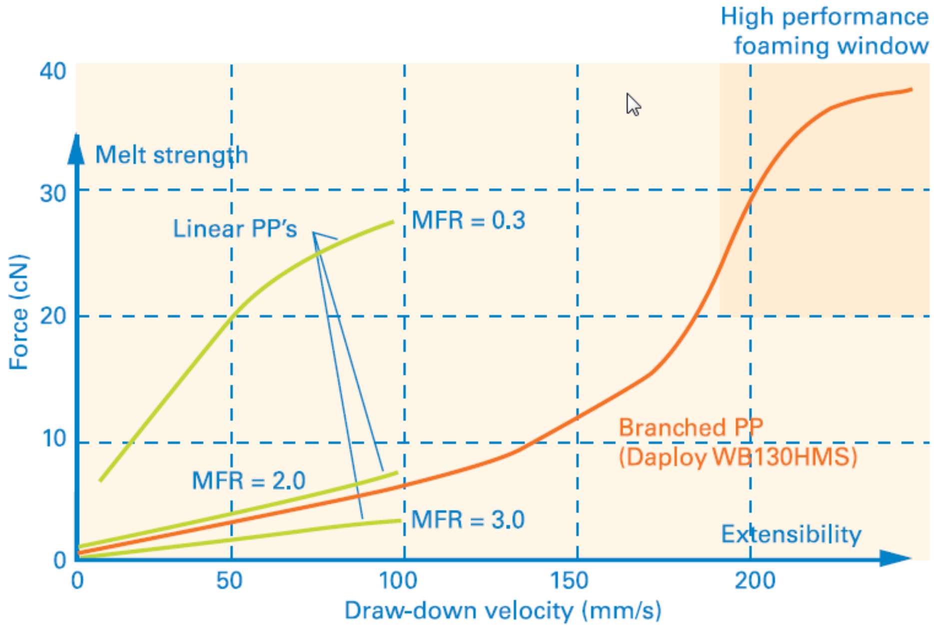
Melt strength

Depends on:

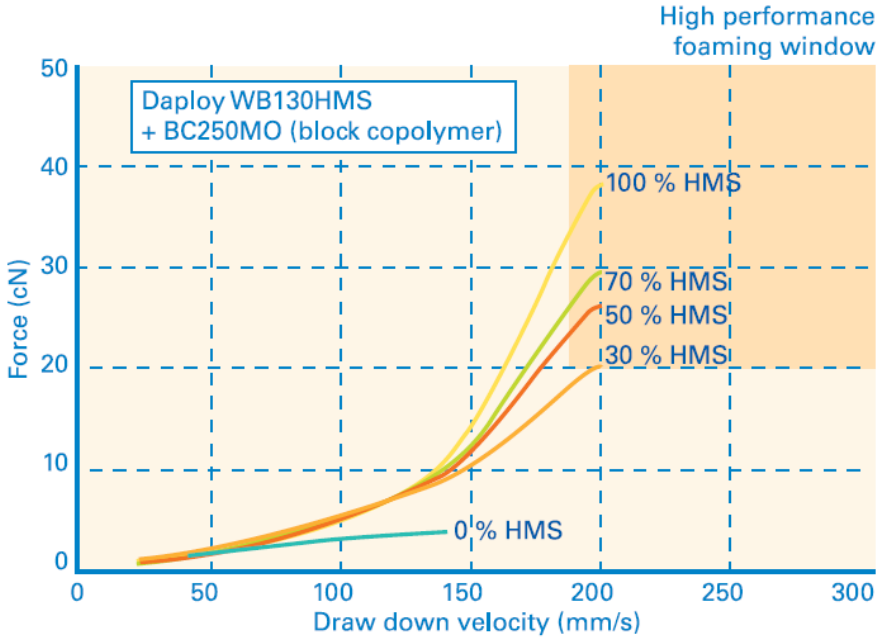
- Molecular weight;
- Molecular weight distribution;
- Chain entanglements;
- Molecular branches;
- Crystallinity.

Optimized by resin supplier!

Melt strength



- Mix of branched and linear good enough for foaming.



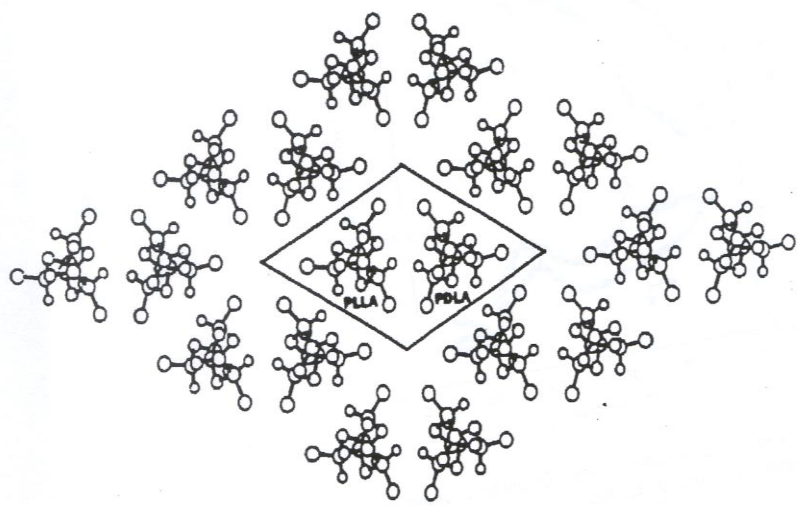
- Increasing melt strength upon decreasing MFI;
- Better foaming upon branching.

Melt strength

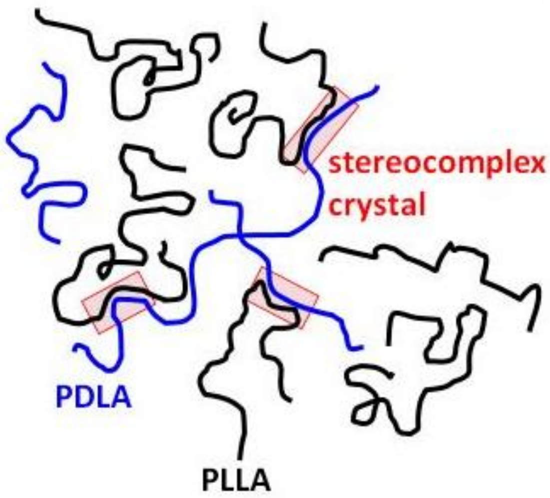
Strategies to change melt strength:

- Increase molecular weight (high MW → higher melt strength → higher die pressure);
- Use chain extenders (Joncryl) or branching agents (peroxide);
- Blend with other polymers (Ecoflex / Vinnex);
- Use special initiators to polymerize branched PLA (WUR-FBR lab and scale up at BEWi-Synbra);
- Increase crystallinity.

Melt strength



- PLLA and PDLA can co-crystallize into stereocomplex PLA (sc-PLA);
- Depends on molecular weight and optical purity of PLLA & PDLA;
- Sc-PLA can nucleate crystallization of hc-PLA.

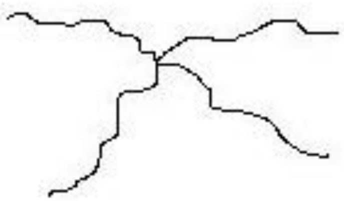


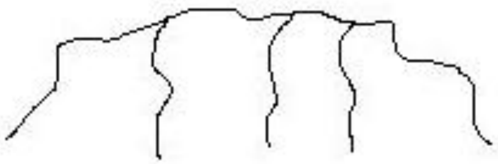
- Use branched PDLA to increase the melt strength of PLA (increased entanglements);
- Use branched PDLA to increase the crystallization of PLA (increased nucleation).

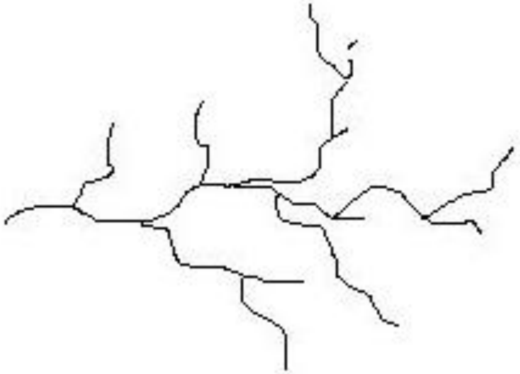
Branched PDLA

New PDLA type:

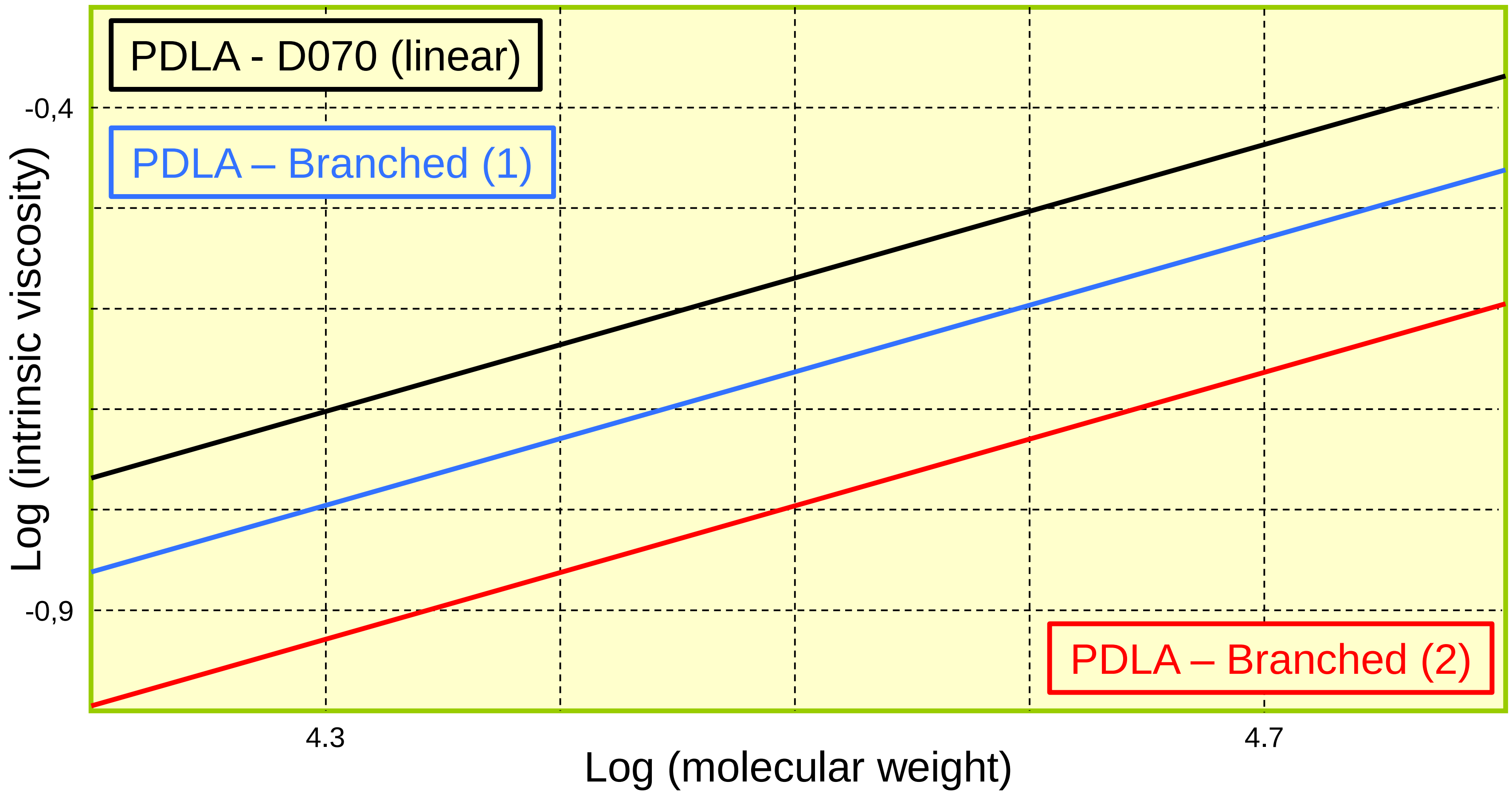
- Star shaped / comb like / hyper branched;
- Large scale production on March 23rd 2017;
  - 400 kg/hr;
  - Multi functional alcohol: 2.0 kg/hr;
  - Several hours of production;
  - Mn ≈ 50 kg/mole (BEWi-Synbra method).







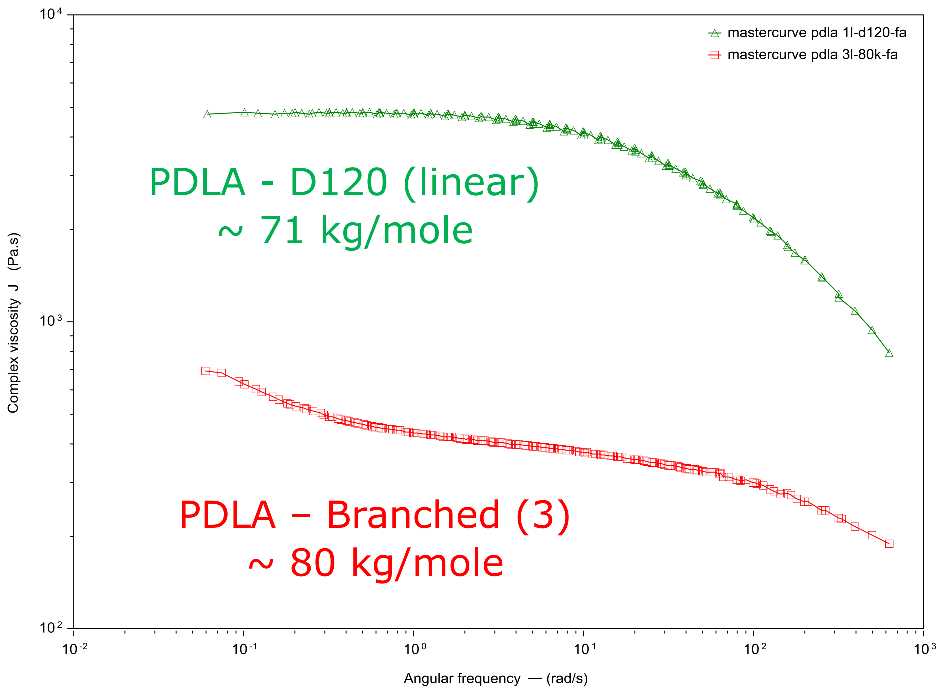
PDLA characterization



Synbra

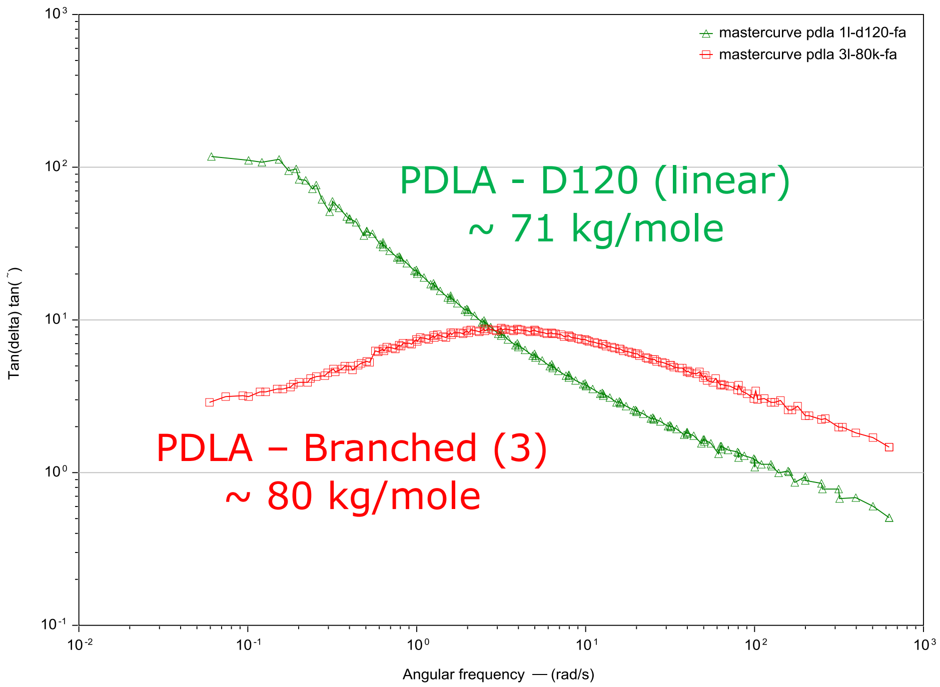
PDLA characterization

BioFoam

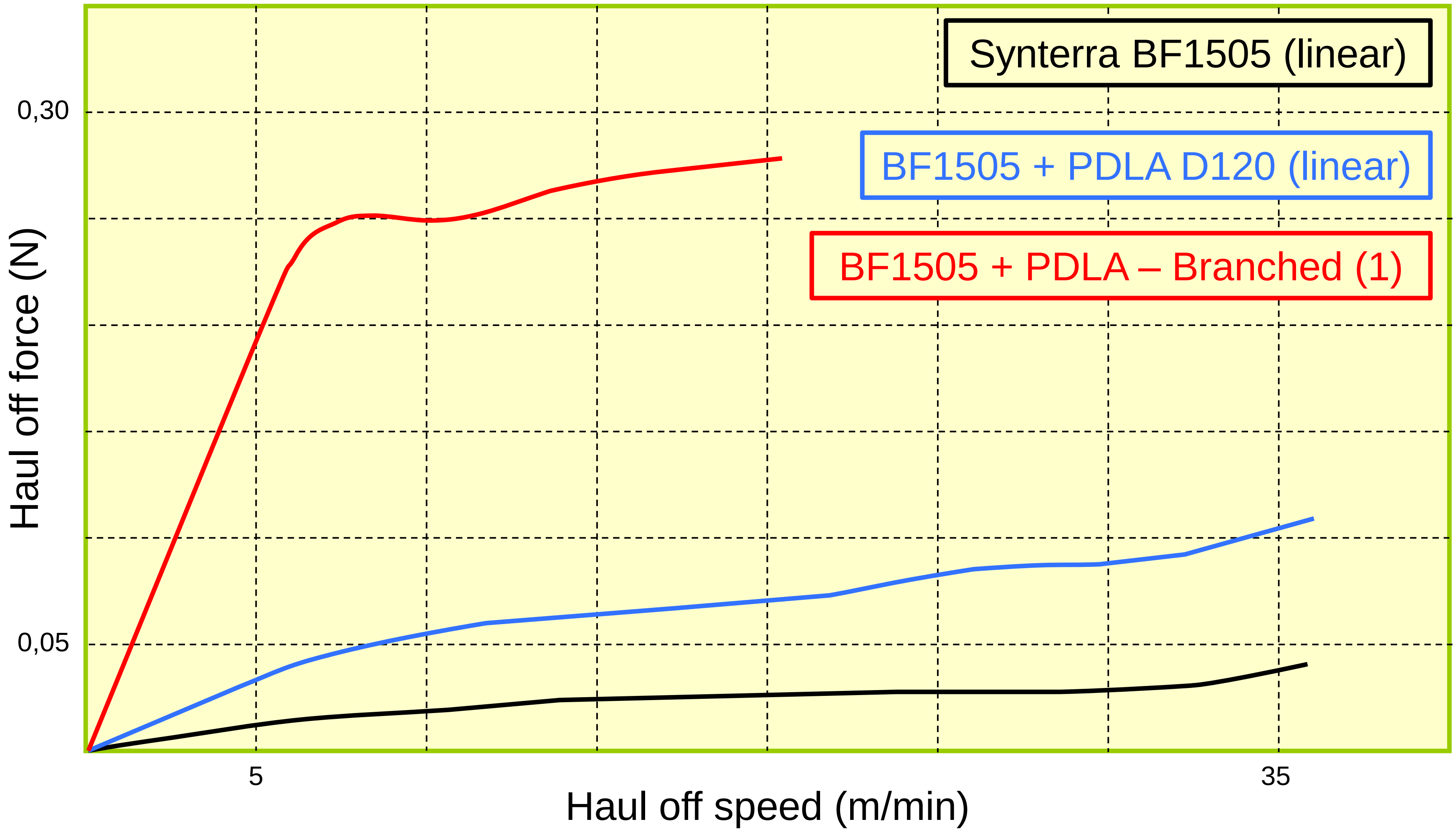


Complex viscosity of branched polymer is lower than of linear polymer.

Tan δ of branched polymer is more constant than of linear polymer.

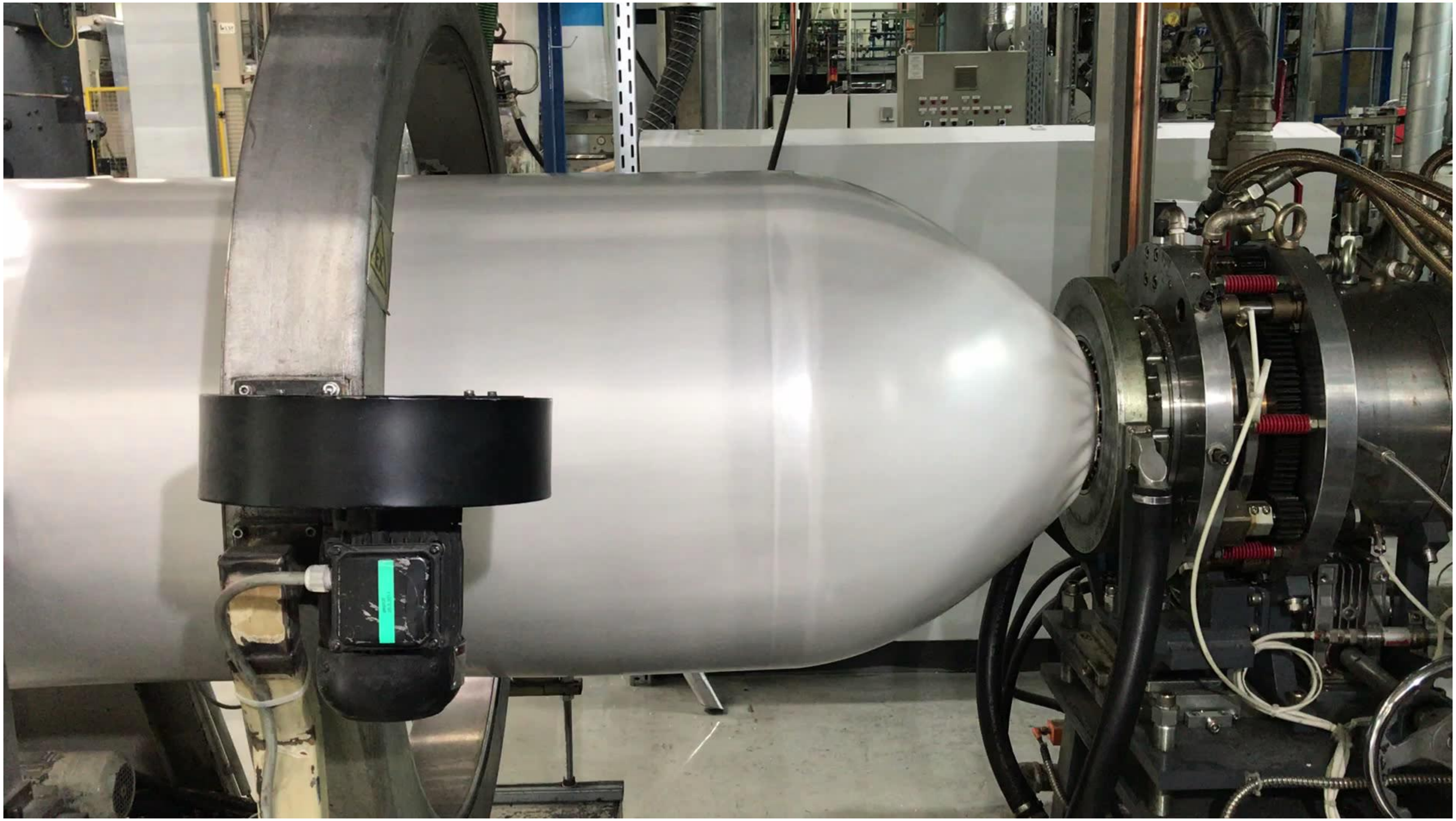


PDLA characterization



Extrusion foaming results

Extrusion foaming results



Conclusions & Future

Conclusions:

- Patent application;
- Industrial scale production of PDLA – Branched (1) at BEWi-Synbra;
- 4 series of foaming trials at Vinventions;
- 3 series of foaming trials at Sulzer;
- Stable extrusion foaming.

Future:

- Other branched PLA types;
- Bead foams (BioFoam).