Biobased Performance Materials Symposium
14 June 2018, Wageningen, The Netherlands

Session: Products
Presentation by: Annet Vrieling - Smit, *Avebe*

Title: **Starch-Poly Ethylene Compounds in Films with improved barrier Characteristics (SPECIFIC)**

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Curriculum:
Annet Vrieling - Smit works at Avebe since 2009. At first she started as researcher chemist, developing and optimising starch derivatives for the paper industry. Next she switched to application specialist within the paper department. She worked mostly on application techniques in coating and barriers for paper. The focus within the paper department of Avebe shifted to food packaging. In this bio-degradable plastics are also very interesting. Therefore, the Specific project with WUR and Sabic became very interesting. Since January she made a shift to the food department, where the first focus is extrusion process and application of potato protein for meat alternatives.

Abstract:
Polyethylene is known for its excellent waterproof properties, but it is permeable to oxygen and other gasses. Starch is a good oxygen barrier, but is not water resistant. A good mixture of both materials should result in products with high water and oxygen barrier.
In this project rheological properties were studied to develop more background knowledge on compounds based on ThermoPlastic Starch (TPS) and polyolefins (specific LDPE) suitable for the film blowing process. Important questions are how the rheology of the system can help us to understand the blend structure. Also how to measure the rheological properties of the blend components such they are representative for the blending process and film structure.

Starch – Poly Ethylene compounds in films with improved barrier characteristics

Annet Vrieling, 14 June 2018

“SPECIFIC” project

- **S**tarch – **P**oly **E**thylene **C**ompounds **I**n **F**ilms with **I**mproved barrier **C**haracteristics

September 2015

December 2017

Innovation by nature

“SPECIFIC” project

Partners:

Innovation by nature

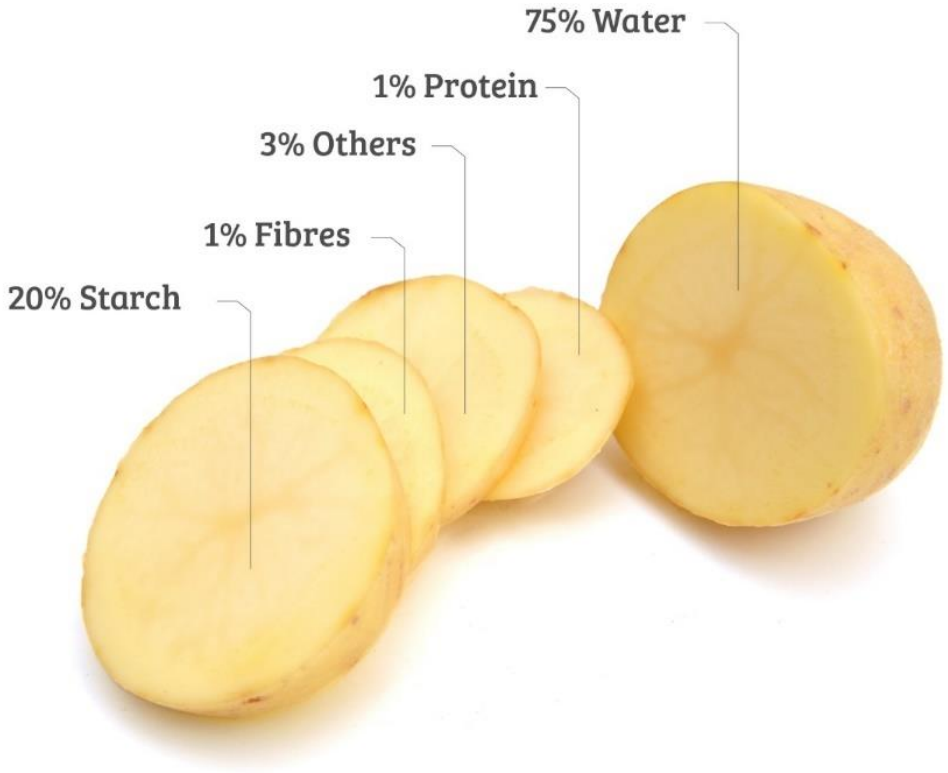
Content

- Introduction Avebe
- Goal Specific project
- Experimental set up
- Results
- Conclusions
- Outlook

We are Avebe

- Founded in 1919 as a farmer's cooperative
- The largest potato starch and derivatives company in the world
- Processing 2.5 million tons of potatoes per year
- Producing of 600,000 tons of starch and starch derivatives per year
- Approximately 2300 members and 1300 employees
- Production facilities in Northwest Europe
- Global sales organisation

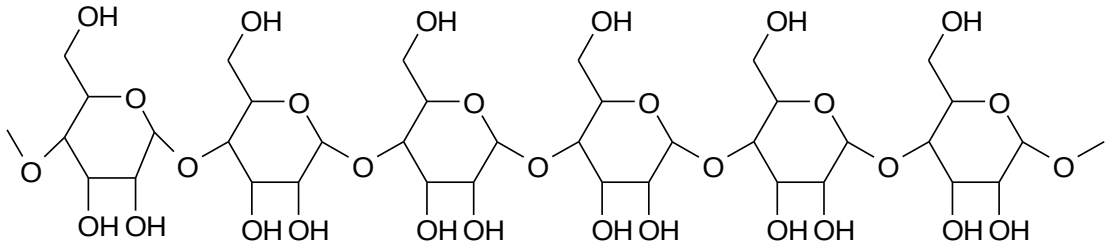
We extract everything to create value

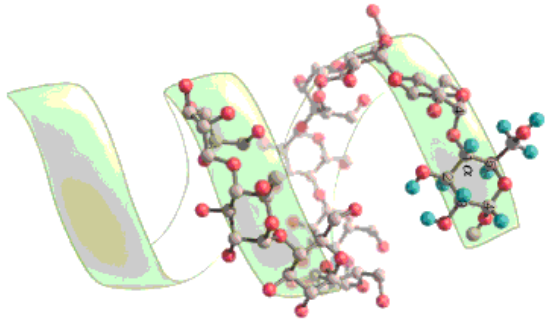


"The potato is one of nature's gifts, and no other company in the world can match our ability to unwrap it."

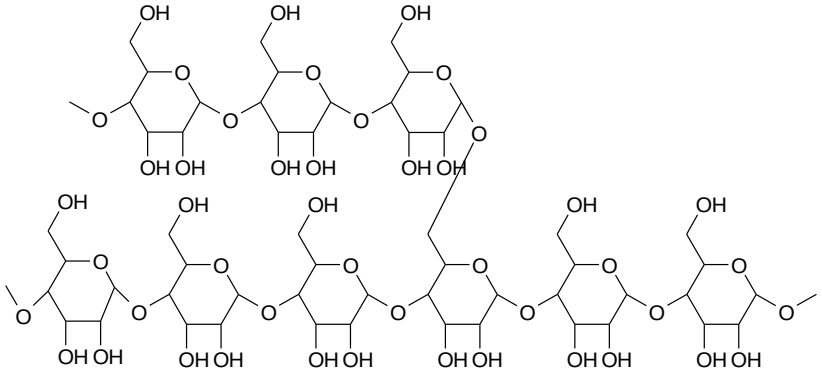
Starch, the polymer

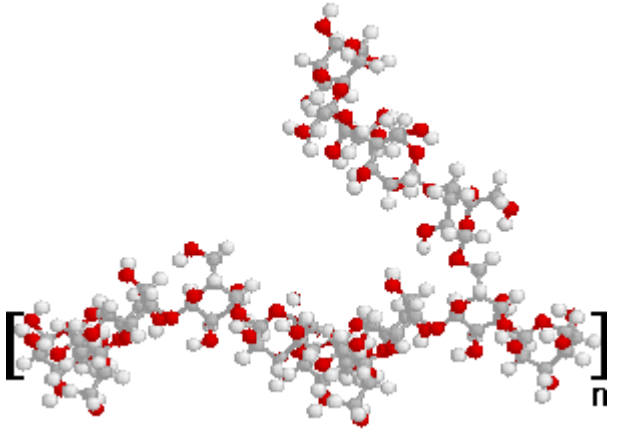
- 20% Amylose and 80% Amylopectin





- Amylose : linear poly-glucoside with α-(1,4) linkages

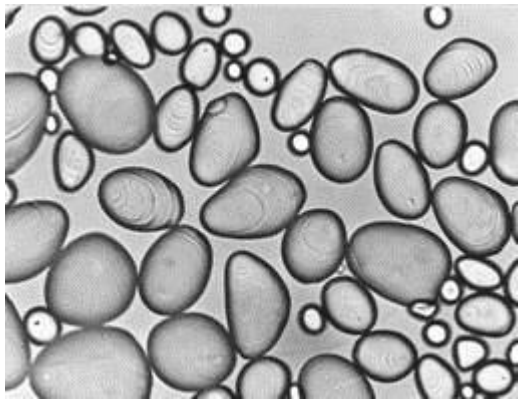




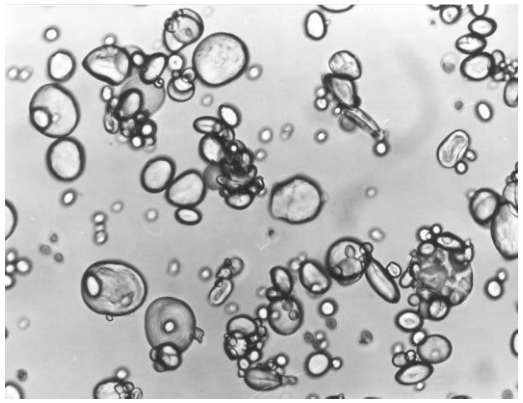
- Amylopectin: highly branched poly-glucoside with α-(1,4) and α-(1,6) linkages

Starch of different botanical sources

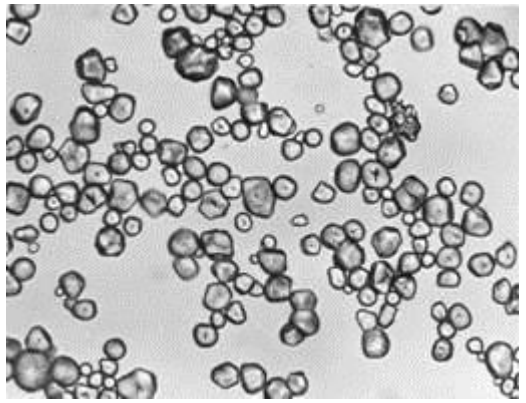
Potato



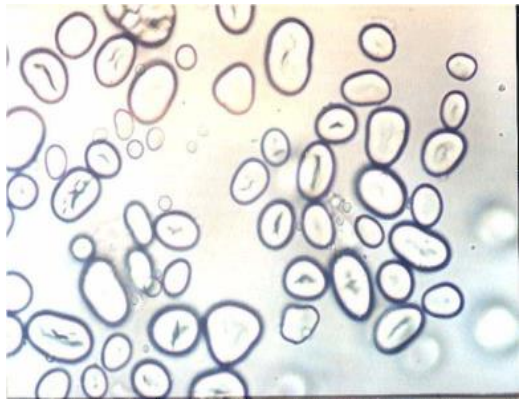
Wheat



Maize



Pea

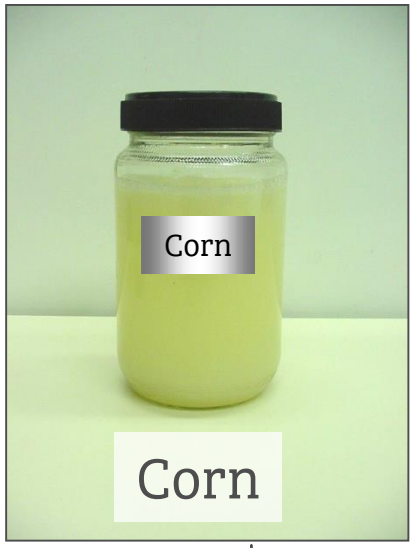


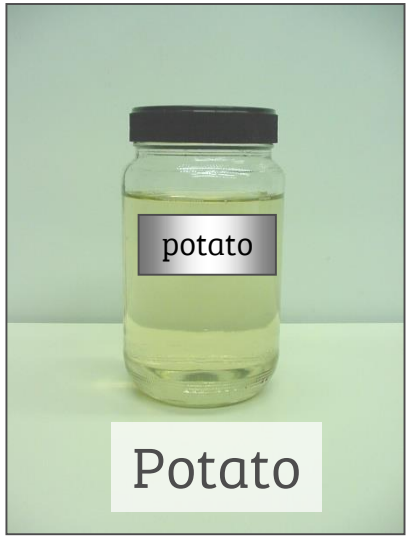
Composition of different native starches

Source	Amylose	Amylopectin	Lipids	Protein	Phosphor	Pasting T	Solub @ 95°C
Potato	21	79	< 0.1	< 0.1	0.08	60-65	82%
Corn	28	72	0.8	0.4	0.02	75-80	25%
Wheat	26	74	0.9	0.4	0.06	80-85	41%

Potato starch

- ✓ Purest from origin
- ✓ Natural anionically charged
- ✓ Easy dissolution





Amylose + lipid = amylose/fat complexes (upto 16%)

Goal Specific project

- Develop film:
  - Good barrier properties
  - Water resistant
- Develop background knowledge on compounds based on a mixture of non-renewable polyolefins and renewable ThermoPlastic Starch (TPS)
- Develop knowledge of the rheology of the system to understand the blend structure
- Learn how the rheological properties of the blend components such that they are representative for the blending process and film structure

System description of the film

Polyethylene

PE is water resistant,
but has poor gas barrier properties

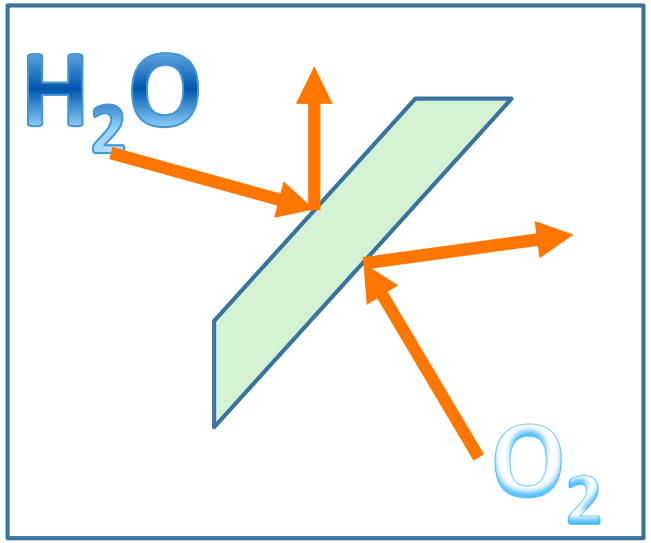
+

Thermoplastic Starch

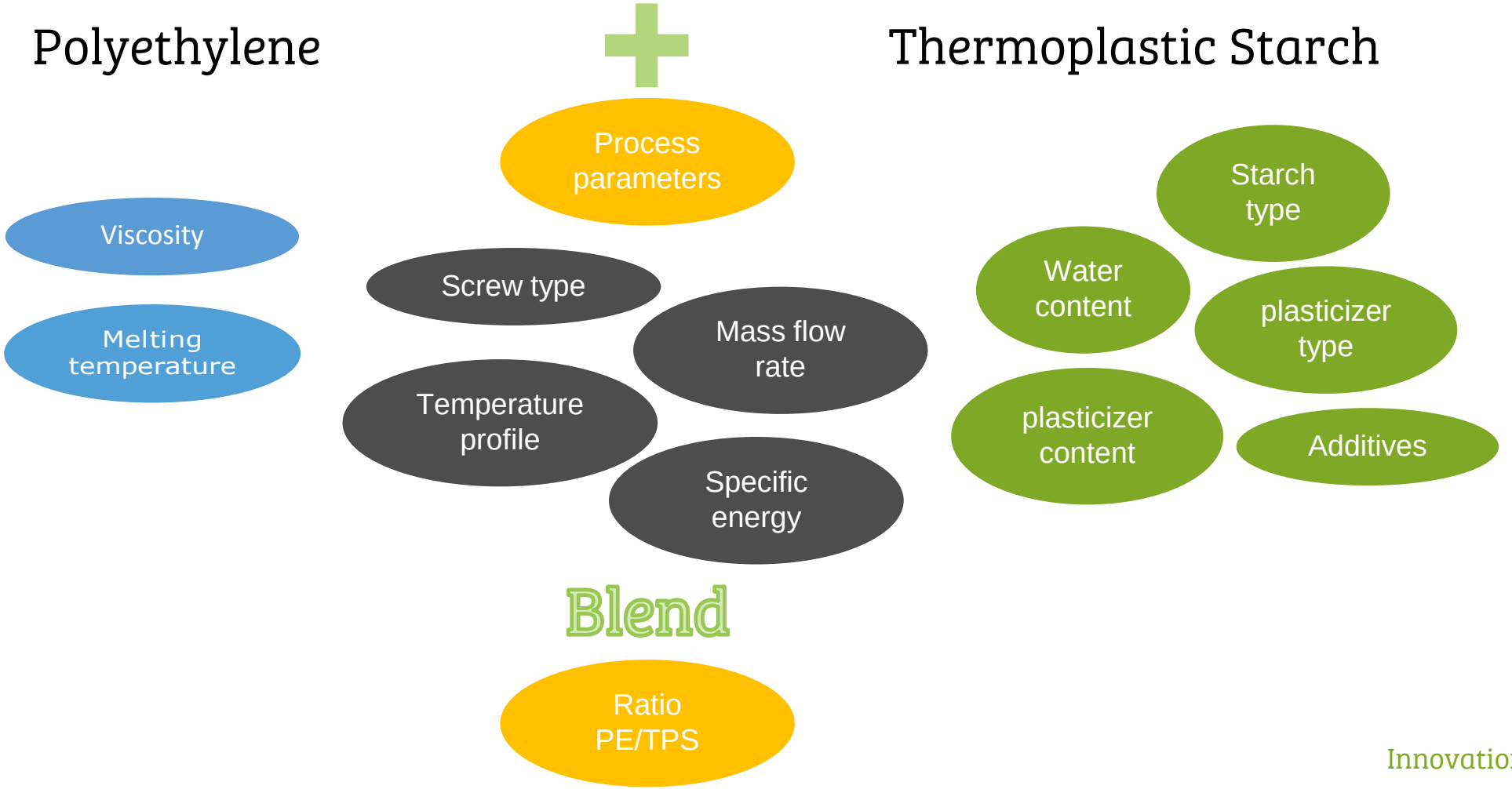
Starch has good barrier properties,
but is water sensitive

Blend

Synergistic effect:
Good barrier properties and water resistant!



System parameters



How to measure the viscosity of TPS?

Capillary rheometer

Rapid Visco Analyser (RVA)

Dynamic rheometer

Content

- Introduction Avebe
- Specific project
- Goal
- Experimental set up
- **Results**
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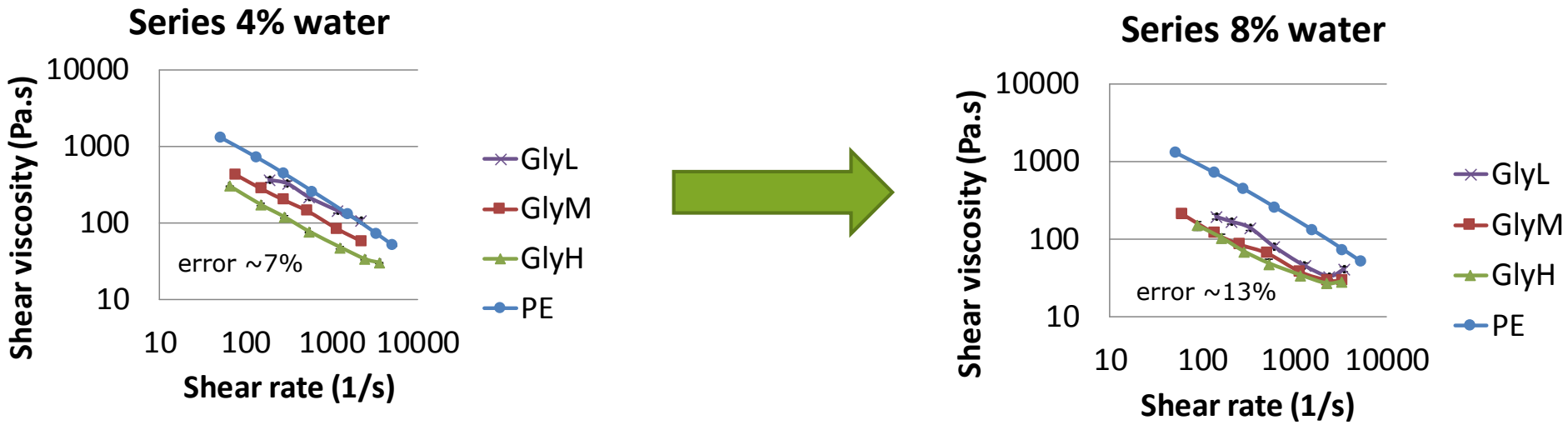
Rheological study of extruded TPS compounds

	Glycerol/ Dry starch	Water content after extrusion [%]			
		A	B	C	D
GlyL	Low	4	8	25	20
GlyM	Medium	4	8	25	20
GlyH	High	4	8	25	20

Suitable TPS samples for capillary and dynamic rheometry

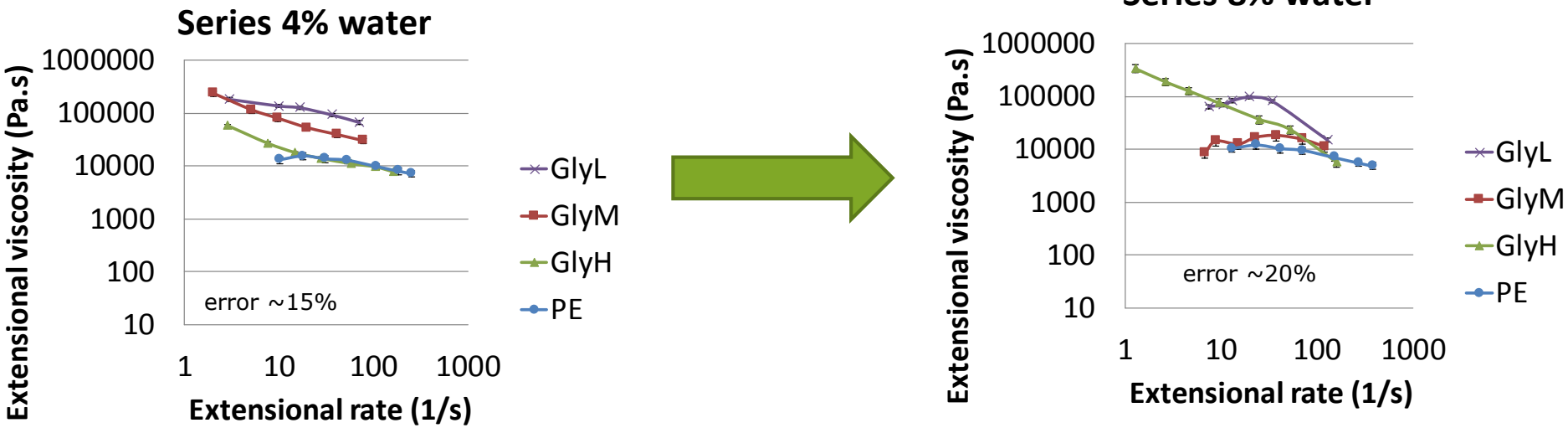
- Possible to compare rheological properties of the individual components of the blends
- The most interesting water contents are the highest because they should resemble conditions in the extruder!

Results capillary rheometry



- Shear viscosity resembles extrusion conditions

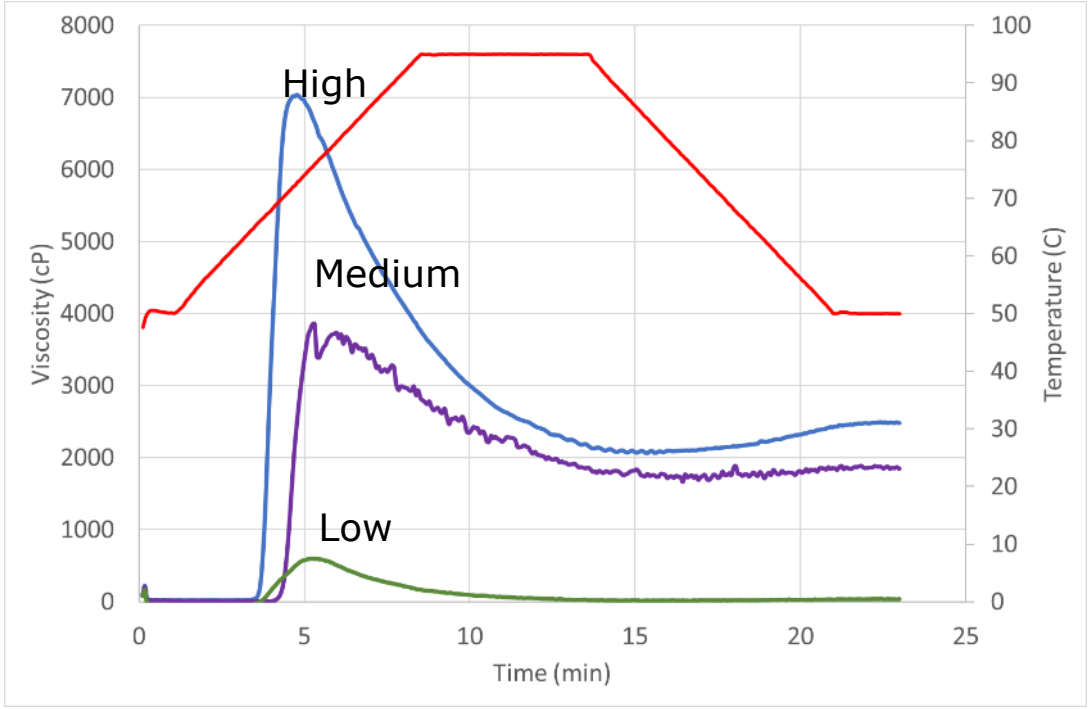
Results capillary rheometry



- Extensional viscosity is important parameter for film blowing process

- Instead of adding more glycerol, what about lower viscous starch types?

Influence starch type on RVA viscosity

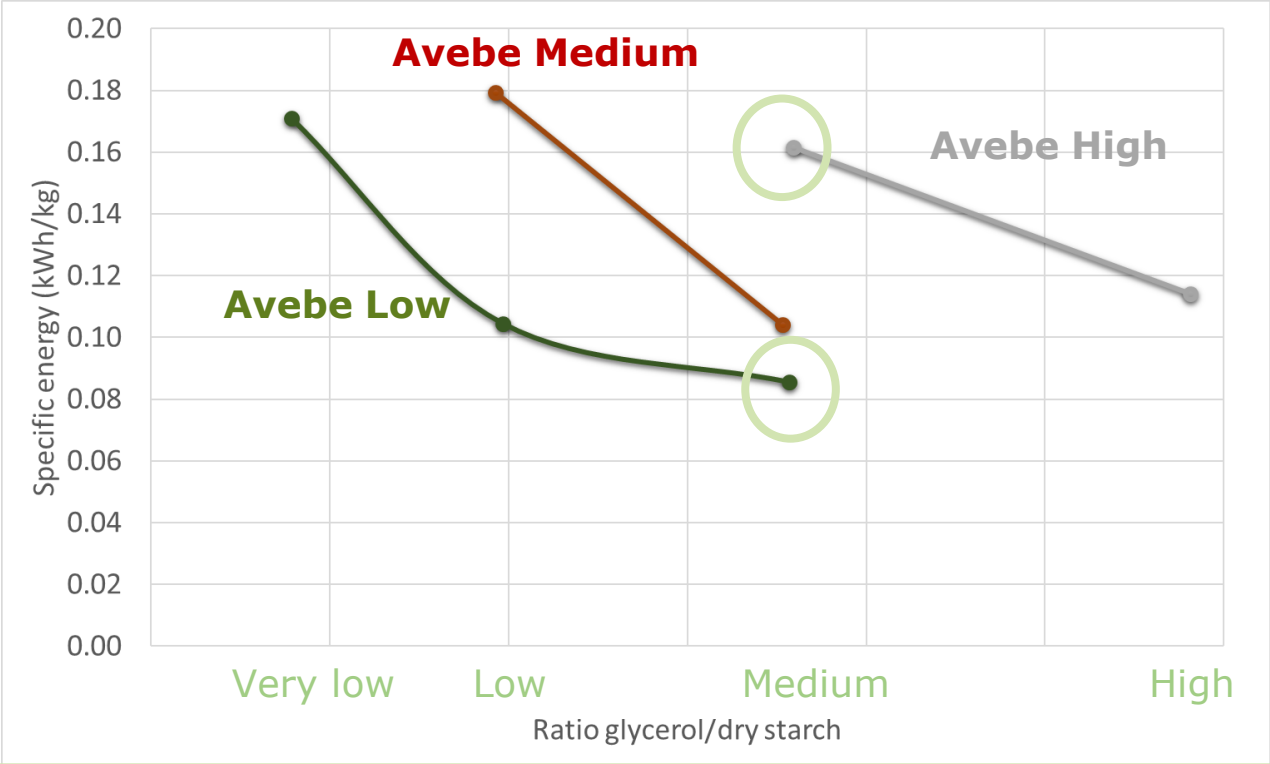


Peak viscosities and end viscosities of starch materials at 3 different levels: high, medium, low.

Higher viscosities require more glycerol for extrusion.

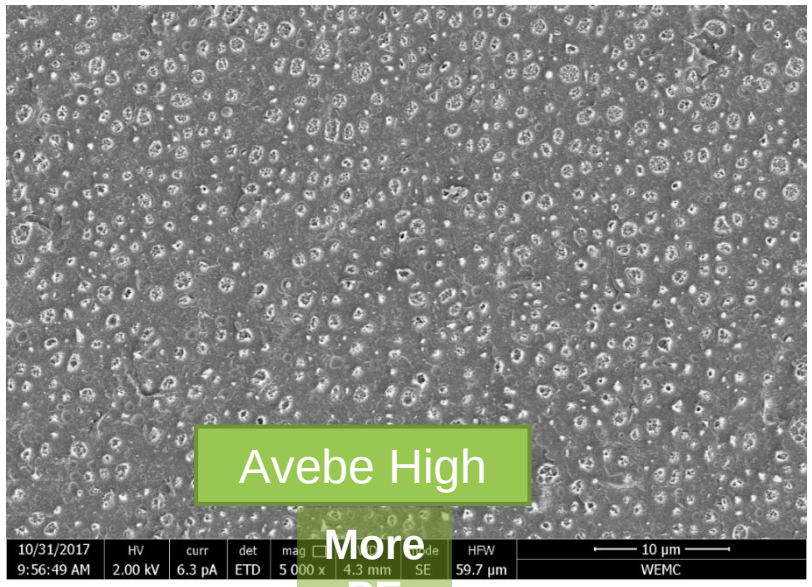
	Peak viscosity	End viscosity	T at Peak visc	Time at peak visc
	(cP)	(cP)	(°C)	(min)
AVEBE High	7034	2479	72.8	4.78
AVEBE Medium	3857	1848	76.0	5.32
AVEBE Low	599	40	75.1	5.18

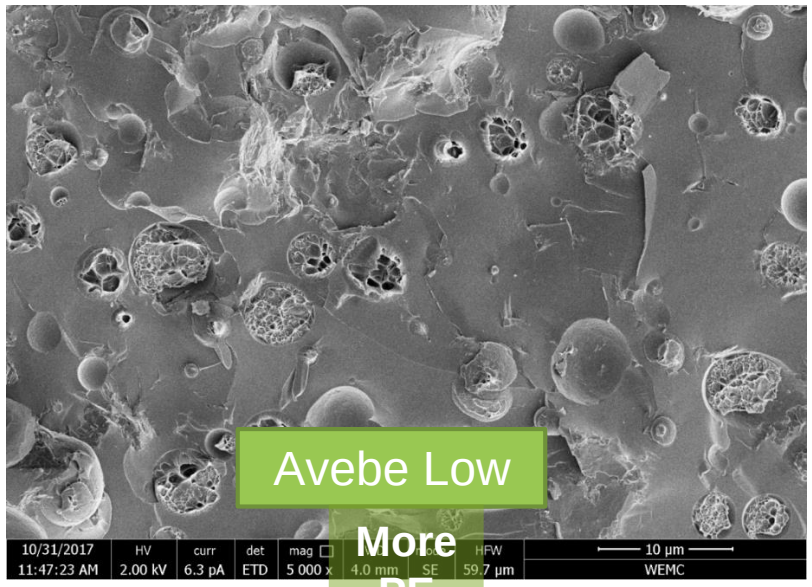
Extrusion results during blending

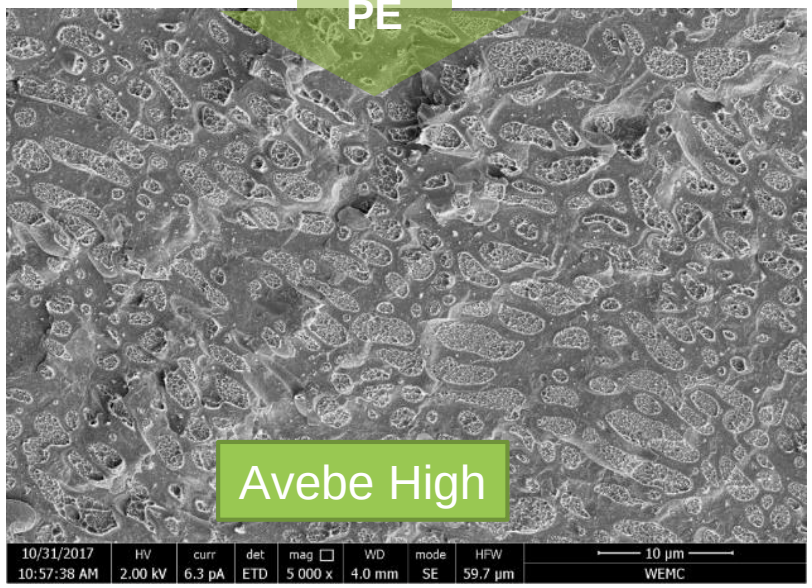


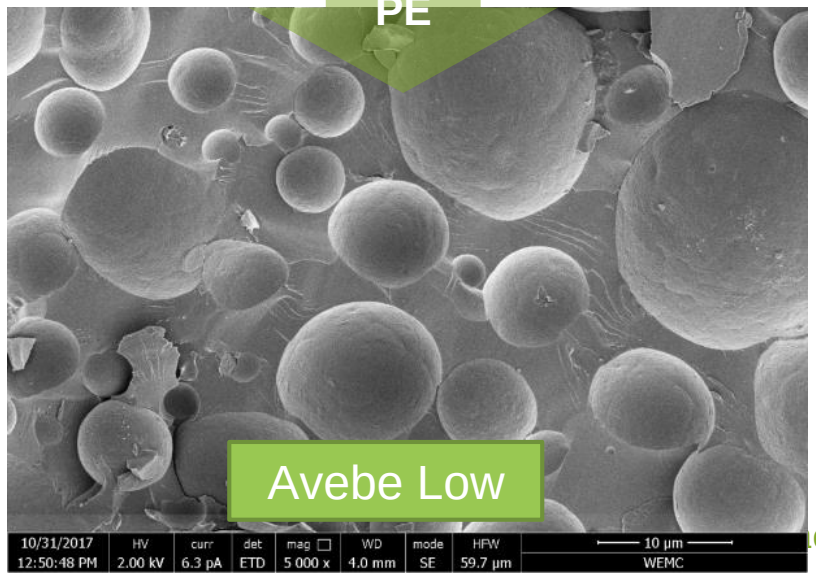
- Decreasing the amount of glycerol for the same starch type increases specific energy
- Varying the type of starch can result in the same specific energy at lower glycerol contents.
- RVA results reflect on the extrusion settings!

Structure in pellets (cryo SEM pictures)









Oxygen transmission rate of films

Avebe high

OTR corrected at 100µm	
23°C, 0%RH	23°C, 70%RH
7.60 [0.32]	1080 [7]

More PE

Avebe high

OTR corrected at 100µm	
23°C, 0%RH	23°C, 70%RH
381.8 [18.3]	1385 [90]

Avebe low

OTR corrected at 100µm	
23°C, 0%RH	23°C, 70%RH
4.35 [0.01]	1278 [170]

More PE

Avebe low

OTR corrected at 100µm	
23°C, 0%RH	23°C, 70%RH
9.65 [0.11]	1358 [105]

OTR: Oxygen Transmission Rate

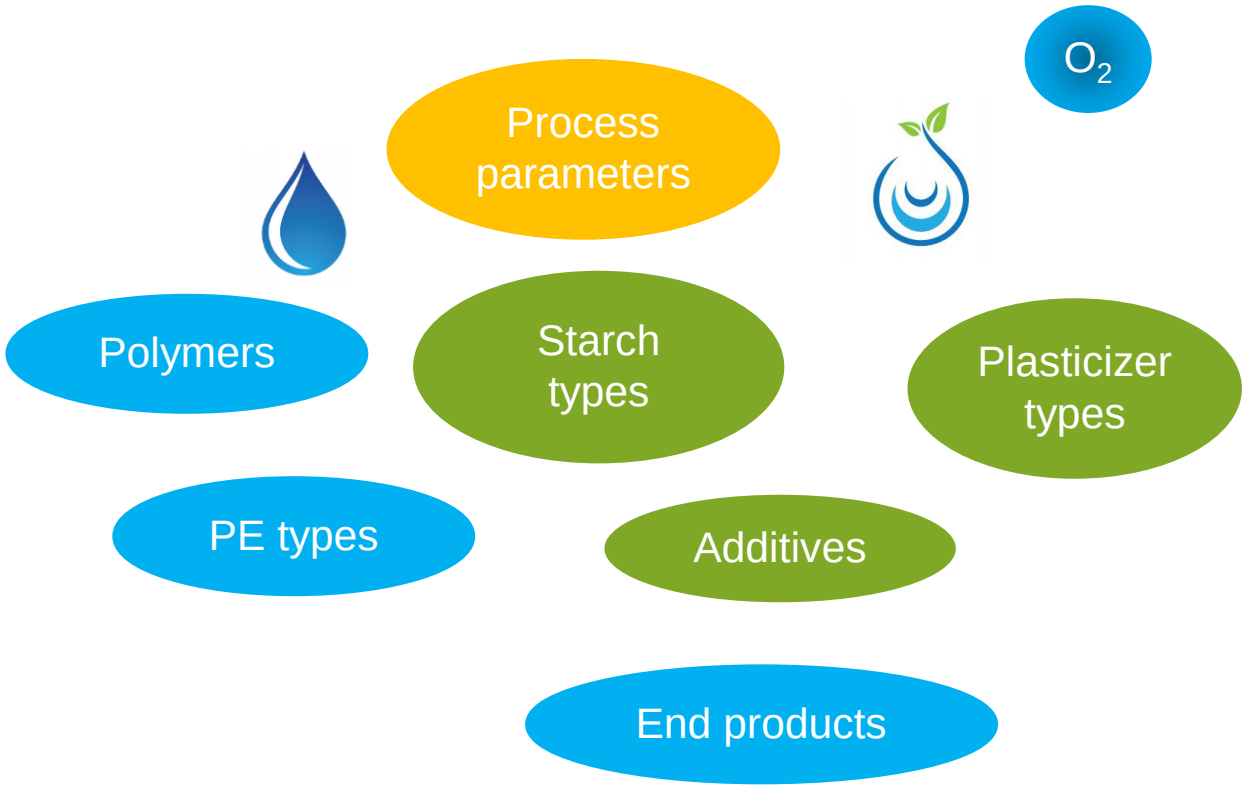
Conclusions

- TPS-PE films is developed with good oxygen barrier properties
- TPS-PE film is still water sensitive
- Changes in rheology of initial materials such as starch type can largely influence the structure of the blend resulting in different film properties!
- Characterizing the rheology of TPS-PE systems is possible at low moisture contents.
- The effect of glycerol in the rheology of the system could be good studied at low moisture contents.

- To be optimised:
- Water sensitivity of the films

Outlook

- Important tools are developed to explore:



Questions ?!

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