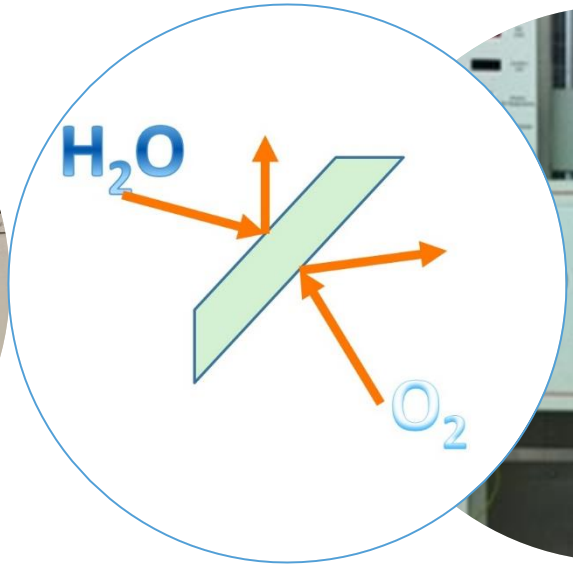
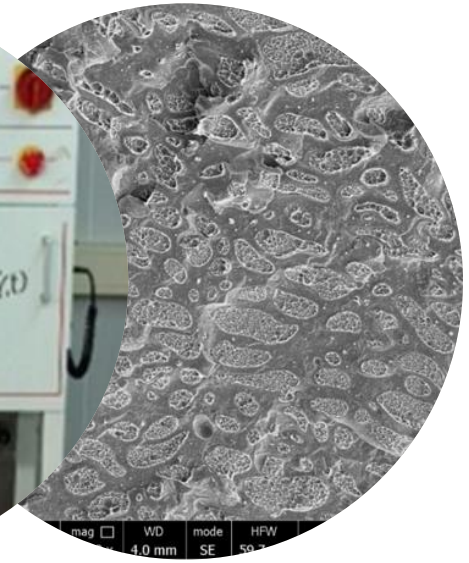
Structure and rheological properties of Starch-PE compounds in film blown applications

Fresia Alvarado Chacon, phD

Wageningen Food & Biobased Research

biobased performance materials





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Outline

- Goal
- PE - Thermoplastic starch systems
- Measuring the rheology of thermoplastic starch
- Effect of glycerol content
- Effect of starch type
- Conclusions

Goal

- How the rheology of the system can help us understanding the blend structure?

- How to measure the rheological properties of the blend components such that they are representative for the blending process and film structure?

System description

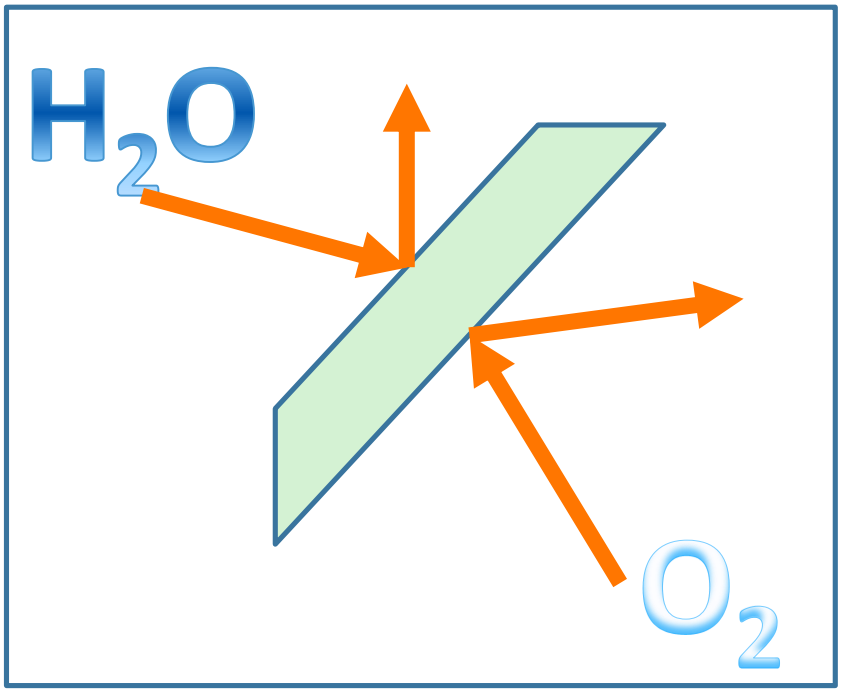
Polyethylene + Thermoplastic starch

PE is water resistant,
but has poor gas barrier properties

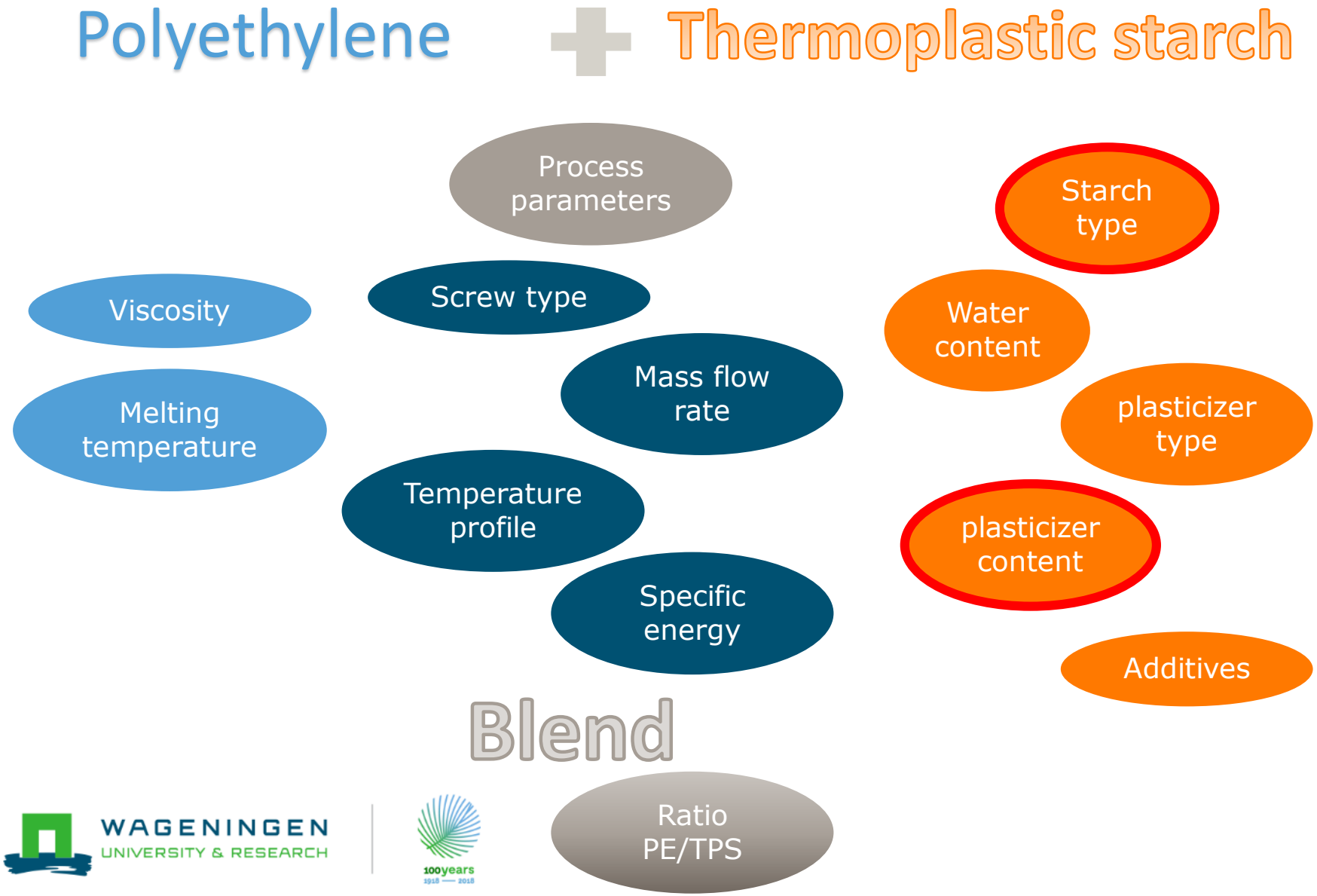
Starch has good barrier properties,
but is water sensitive

Blend

Synergistic effect:
Good barrier properties and water resistant!



System parameters



How to measure the rheology of TPS?

Rapid Visco Analyser (RVA)

Capillary rheometer

Dynamic rheometer

Option 1: Rapid Visco Analyser (RVA)

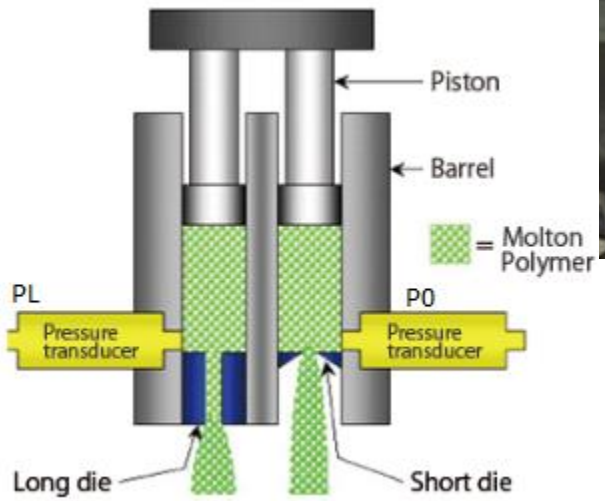
- RVA: typically used for starch viscosity
  - Good in mixing of gelling media
- Temperature profile (e.g. 50-95-50°C in 23 min)
  - Cold viscosity (solubility)
  - Gelatinisation peak
  - Hot viscosity
  - End viscosity
- Composition for TPS representative samples: starch, glycerol, water
- Not possible to analyse PE

Advantages:
1. Uses small sample size
2. Short testing time
3. Ability to modify testing conditions

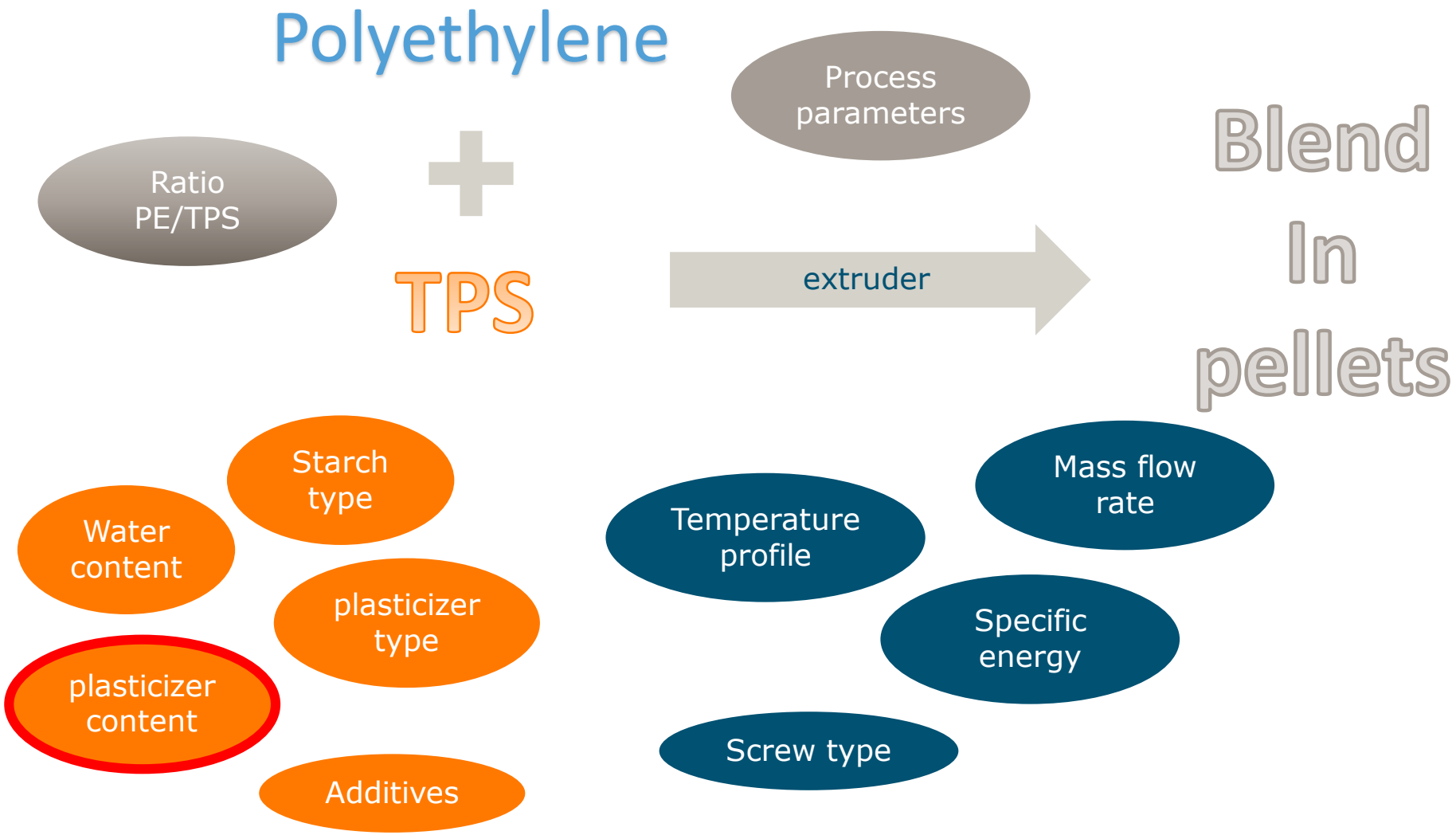
Option 2: Capillary rheometer

It measures:
- shear viscosity
- elongational viscosity (calculated-Cogswell method)

Characteristics:
- Closed system (no water loss during measurements)
- High deformation rates
- No sample preparation, pellets are enough
- Temperatures comparable to extrusion conditions
- Not possible to measure very low viscosities



Effect of glycerol content



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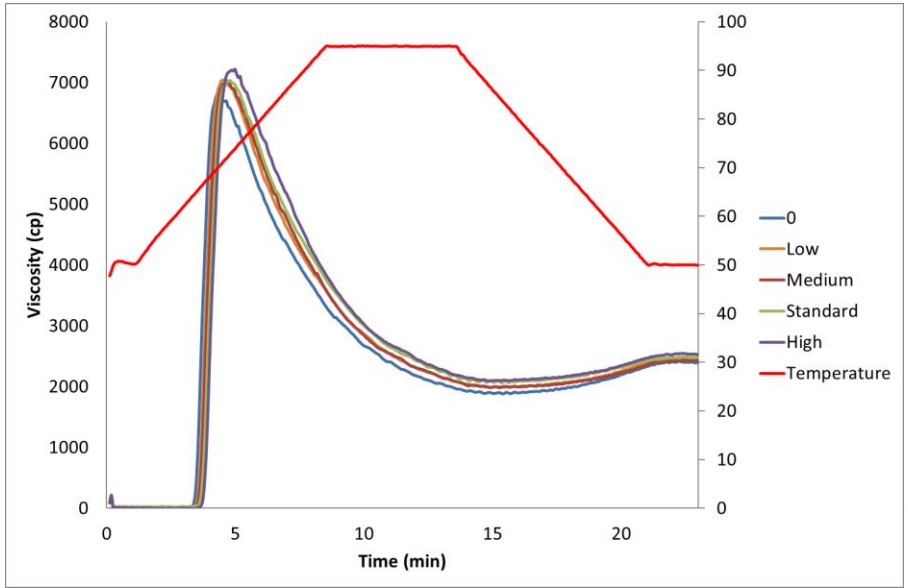
Effect of glycerol on starch viscosity

Ratio glycerol/ dry starch	Peak viscosity (cP)	End viscosity (cP)	Time at peak viscosity (min)	Temperature at peak viscosity (°C)
0	6846	2388	4.38	70.35
Low	7048	2455	4.52	71.15
Medium	7029	2435	4.65	71.90
Standard	7034	2479	4.78	72.75
High	7217	2524	4.98	73.85

- Adding High ratio glycerol to dry starch increases peak and end viscosity only by 5%.
- The time needed to reach peak viscosities shifts less than a minute and the temperature increases by 3 degrees.



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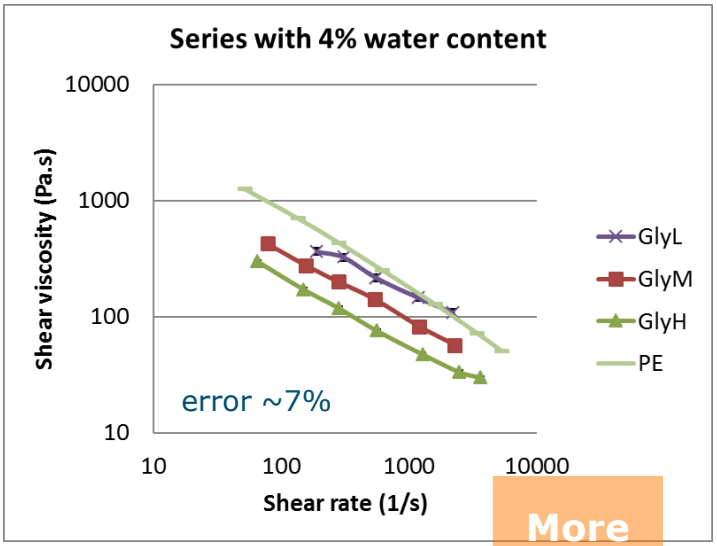
Extruded TPS compounds at different water contents

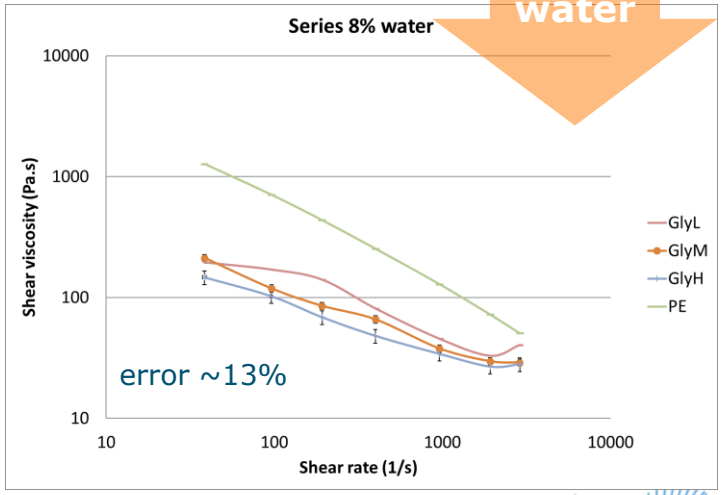
	Sample code	Glycerol/ Dry starch	Water content after extrusion [%]			
			A	B	C	D
GlyL	270716 IV	Low	4	8	25	20
GlyM	270716 II	Medium	4	8	25	20
GlyH	270716 III	High	4	8	25	20

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



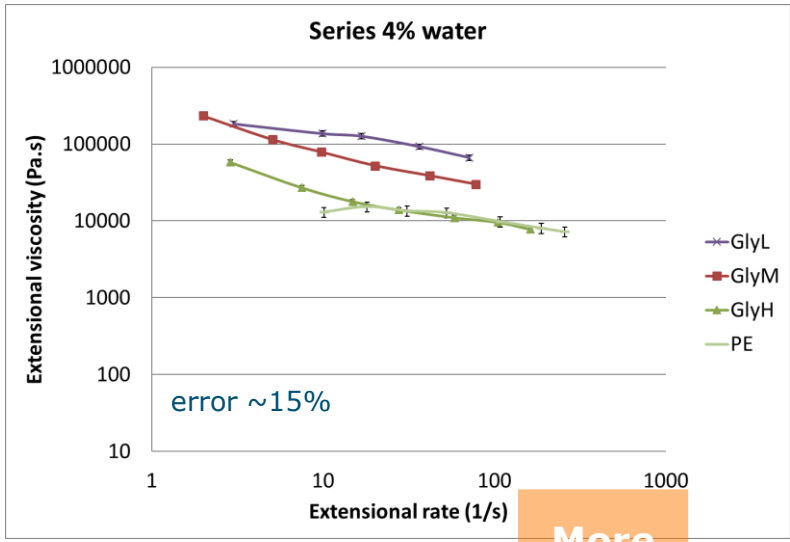


More water

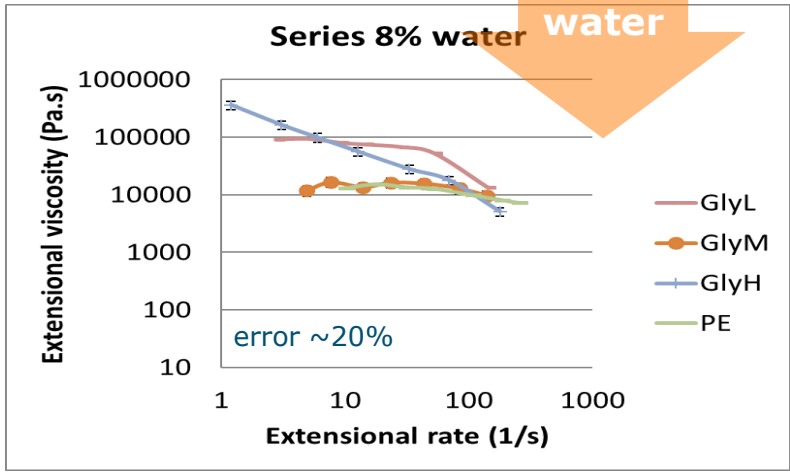
Higher water content → lower shear viscosities, higher errors → **Not possible to measure higher water contents!**

Higher glycerol content → lower shear viscosity (positive for blend processing)
→ extensional viscosity comparable to PE (positive for blend structure)

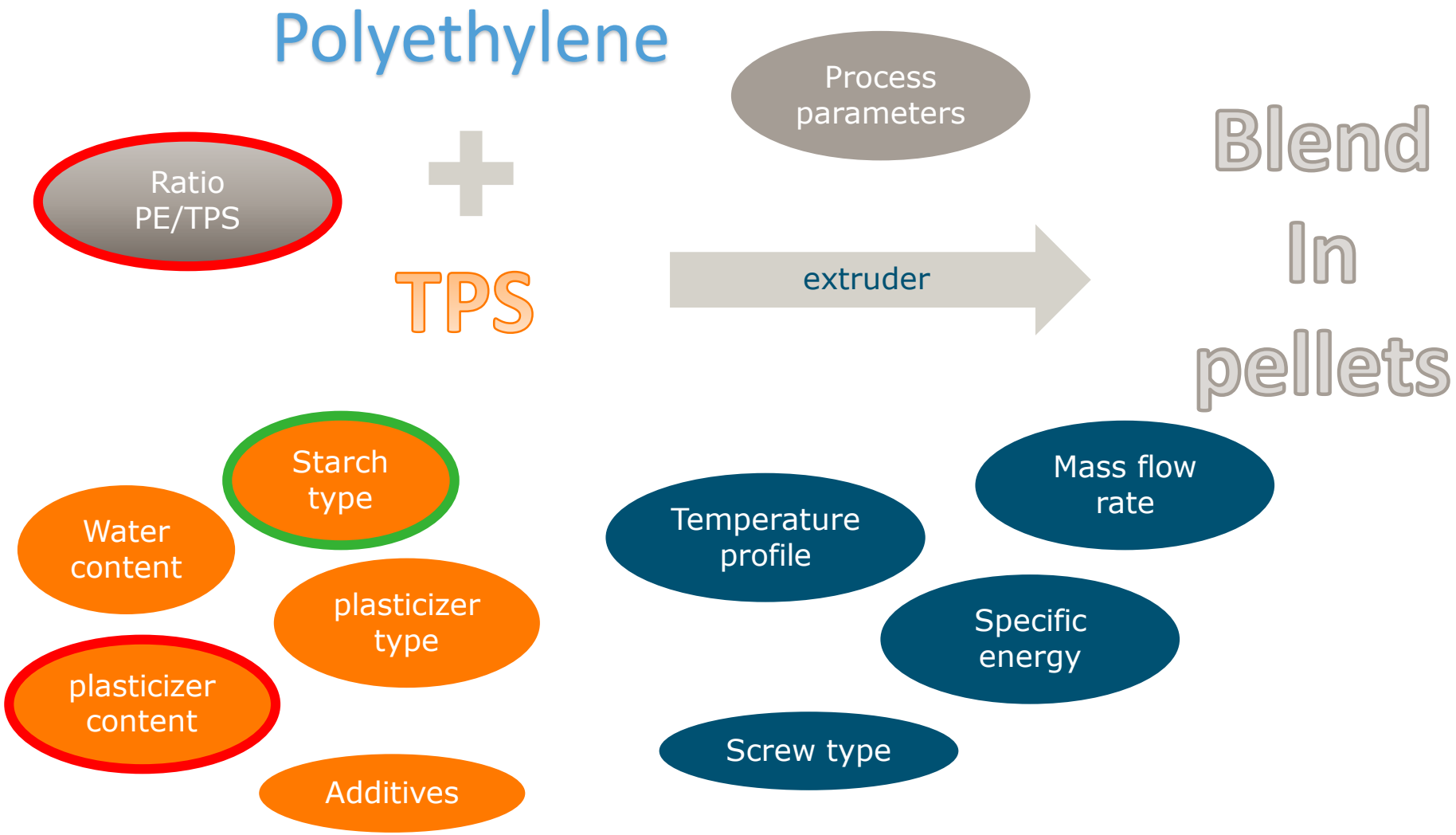
Instead of adding more glycerol, what about starch types with lower shear viscosities ?



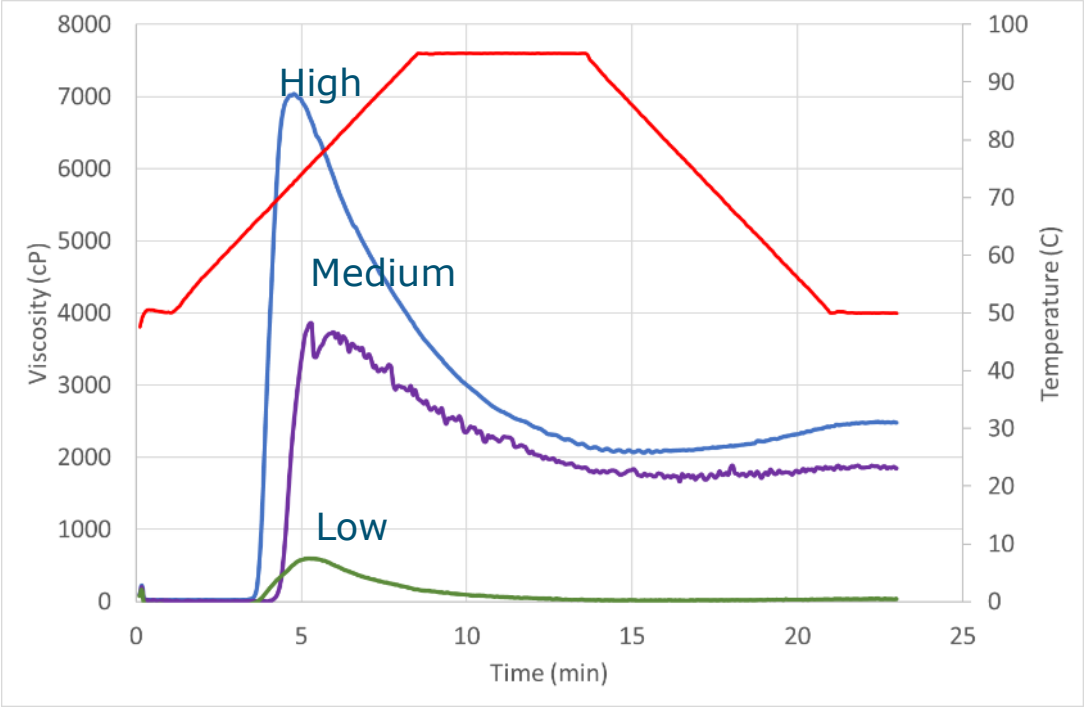
More water



Effect of starch type



Results RVA



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

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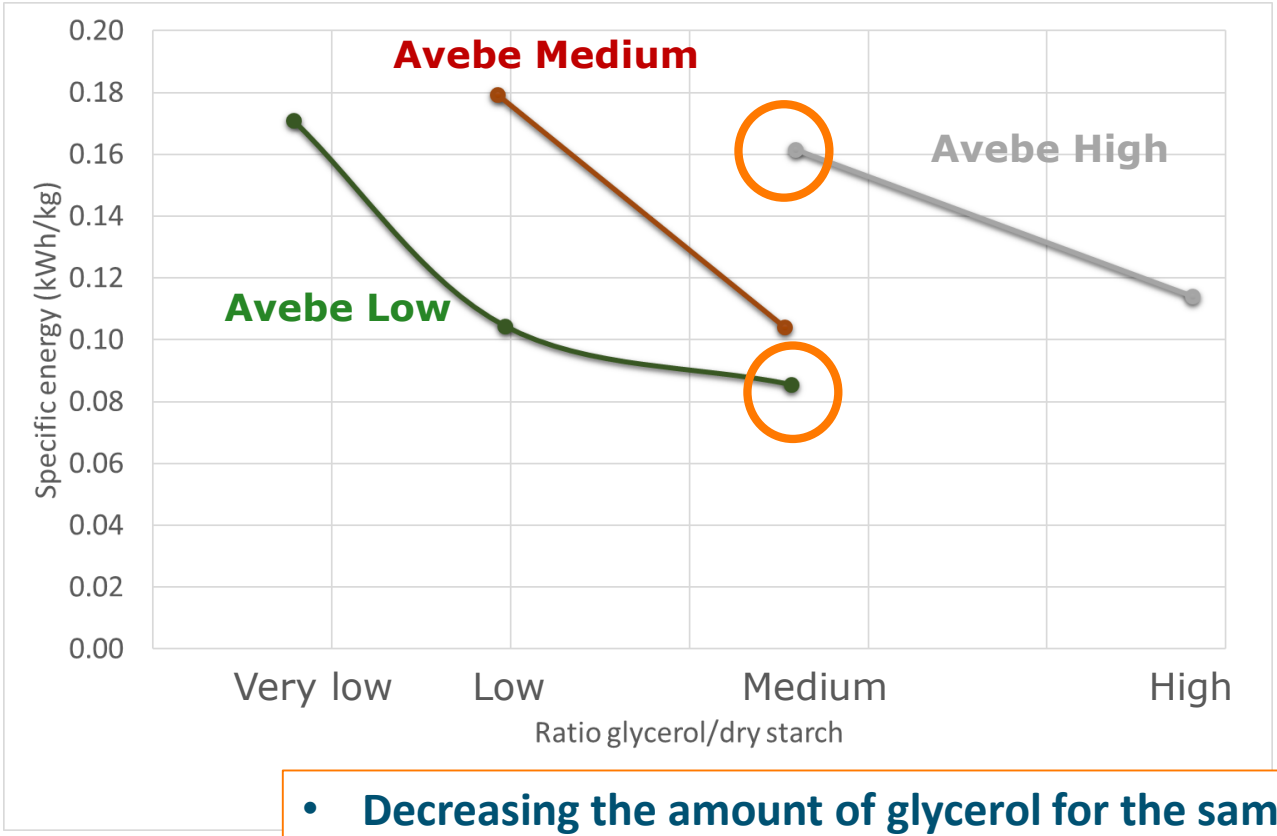
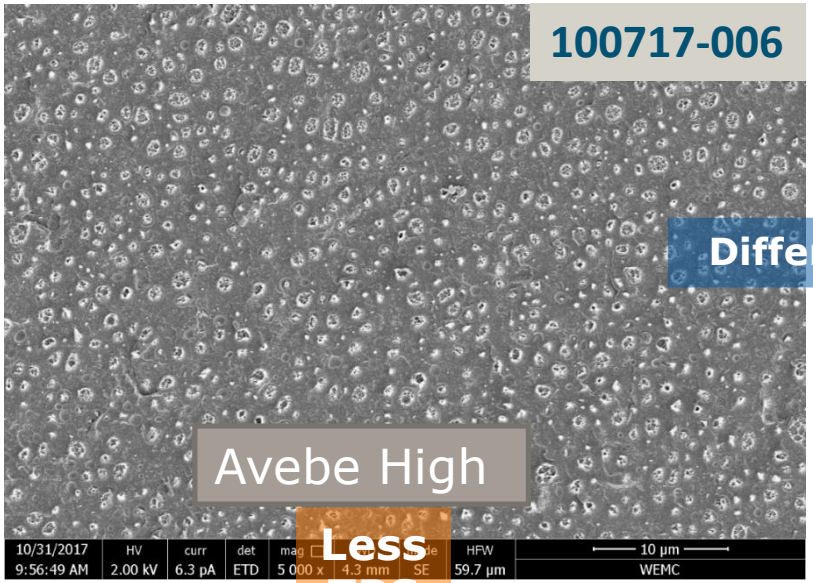
Extrusion results during blending

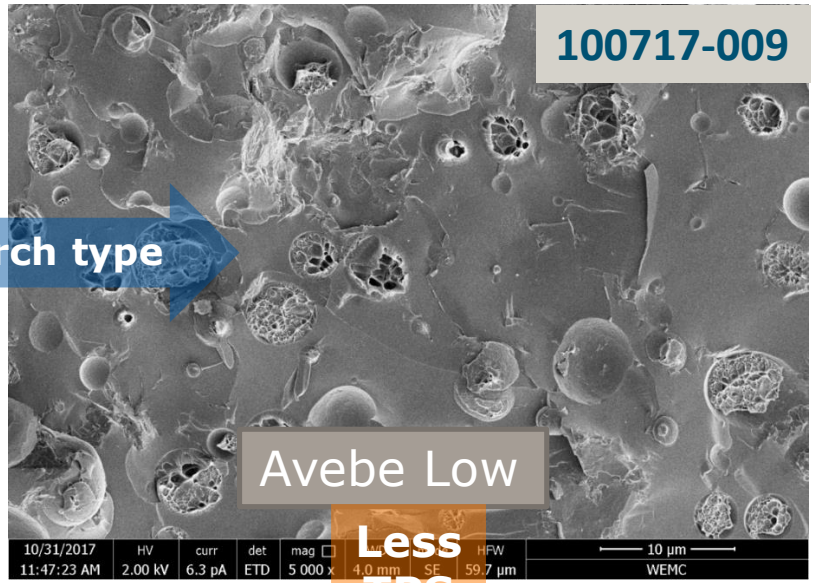


- **Decreasing the amount of glycerol for the same starch type increases specific energy**
- **Varying the type of starch can result in the same specific energy at lower glycerol contents.**
  Glycerol in low V starch < medium < high
- **RVA results reflect on the extrusion settings!**

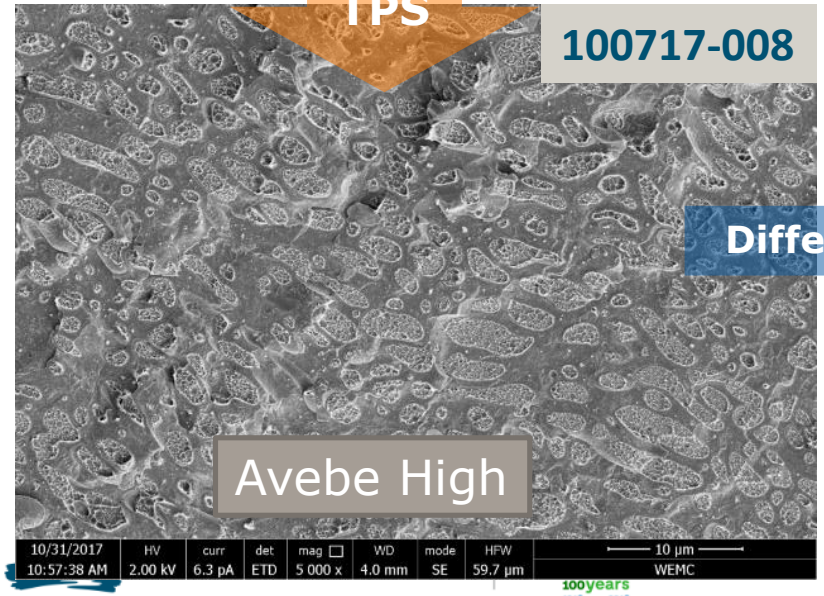
Structure in pellets (cryo SEM pictures)



Different starch type

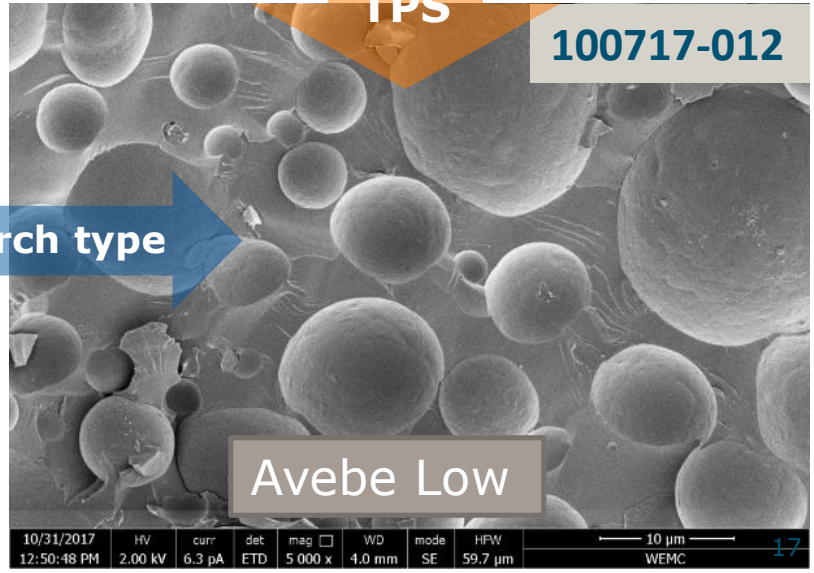


Less TPS



Different starch type

Less TPS



Barrier properties in films

Avebe high

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

Different starch type

Avebe low

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

Less TPS

Less TPS

Avebe high

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

Different starch type

Avebe low

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

Conclusions

- Characterizing the rheology of TPS-PE systems is challenging but possible at low moisture contents.
- The effect of glycerol in the rheology of the system could be good studied only at low moisture contents, therefore the predictive potential of the method could not be confirmed.
- Changes in rheology of initial materials such as starch type can largely influence the structure of the blend resulting in different film properties!

Questions ?!

WFBR: Brigit Beelen,
Herman de Beukelaer,
Gerald Schennink
Clement Fosse
Maxence Paillart

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Avebe

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