Einfluss der Modifikation von Polysacchariden auf die Rheologie von selbstverdichtendem Beton und Mörtel

Influence of the modification of polysaccharides on the rheology of self-compacting concrete and mortar

Wolfram Schmidt

BAM Bundesanstalt für Materialforschung und -prüfung

Use of polymeric stabilising agents

- **Polymeric stabilising agents are often used in cementitious systems**
  - **to avoid bleeding and segregation**
  - **to modify the rheology of mortars and plasters**
- **In normal concrete they are seldomly used**
- **In SCC they are more commonly used**
  - **depending on „SCC culture or tradition“**
  - **to improve the robustness against water variations**
  - **to modify rheological properties**

Influence of stabilising agents on yield stress

- **Most often they are referred to as VMA or VEA**
- **However, typically they affect both, viscosity and yield stress**

400 Liter SCC + 1,2 Gramm ST

Influence of stabilising agents on yield stress

- **Most often they are referred to as VMA or VEA**
- **However, typically they affect both, viscosity and yield stress**

$\eta_{Rheometer}$	≈ 58 Pa s
$t_{V\text{-}Funnel}$	≈ 7 s

400 Liter SCC + 1,2 Gramm ST

$\eta_{Rheometer}$	≈ 85 Pa s
$t_{V\text{-}Funnel}$	≈ 9 s

Influence of stabilising agents on yield stress

- **Most often they are referred to as VMA or VEA**
- **However, typically they affect both, viscosity and yield stress**

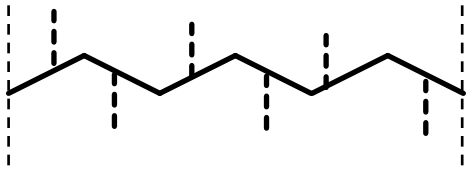
$\tau_{LCPC\text{-}Box}$	≈ 42 Pa
$\tau_{slump\ flow}$	≈ 22 Pa
$\tau_{Rheometer}$	≈ 32 Pa

400 Liter SCC + 1,2 Gramm ST

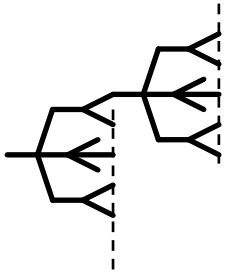
$\tau_{LCPC\text{-}Box}$	≈ 71 Pa
$\tau_{slump\ flow}$	≈ 69 Pa
$\tau_{Rheometer}$	≈ 58 Pa

Common types of stabilising agents

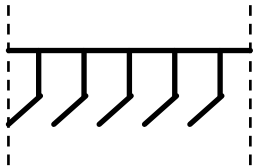
- **Typically used polymeric stabilising agents for cementitious systems are polysaccharides:**
  - **Modified cellulose like HPMC, HEC, CMC**



  - **Modified starch like potato starch, corn starch**



  - **Microbial or biological polysaccharides like Welan gum, Diutan Gum (biopolymers)**



- **Normally they are non-ionic or anionic**

Mode of operation of stabilising agents

- **According to Khayat*, their mode of operation can be distinguished between:**
  - **Adsorption - Adhesion to water molecules, reducing mobility**
  - **Association - Polymers form network**
  - **Intertwining - Polymers entangle particles**

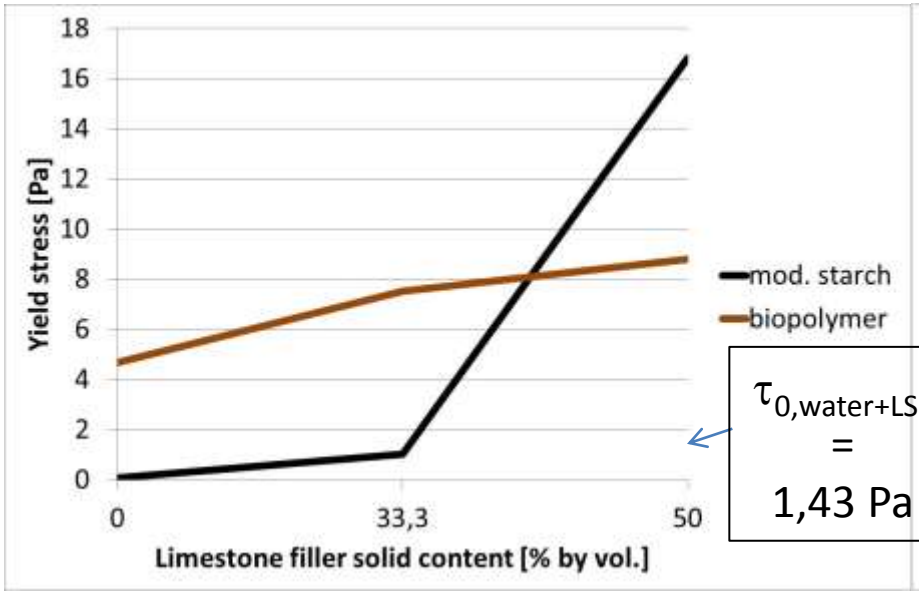
→ **Effect of stabilising agent depends on**
- → **type of polymers**
- → **amount of polymers**
- → **water-solid ratio**

- **Considering modified starch, this list should be amended by**
  - **„Spacing“ - Particles are kept in distance**

* **K. H. Khayat, "Viscosity-enhancing admixtures for cement-based materials -- An overview”, Cement and Concrete Composites, vol. 20, pp. 171-188, 1998**

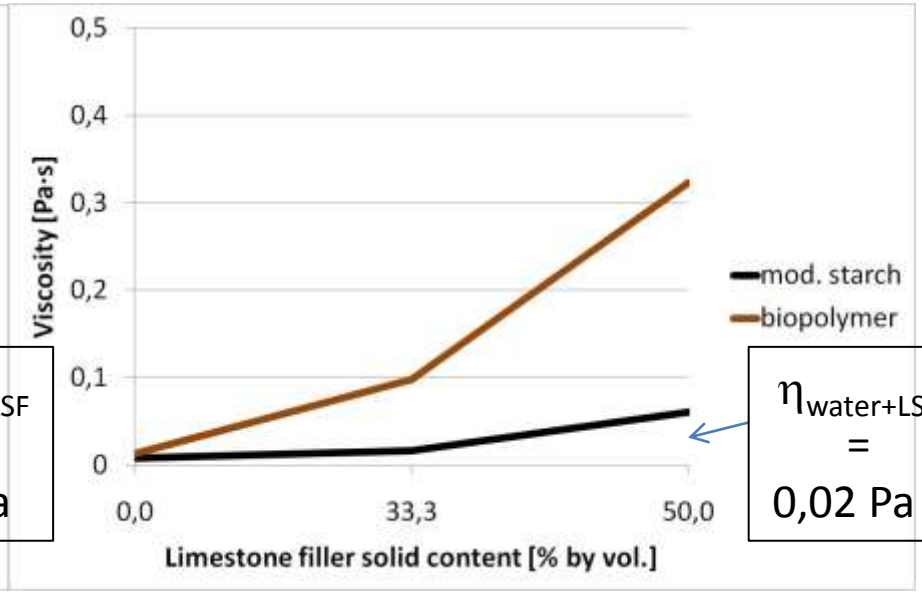
Influence of the amount of particles

Yield stress vs. solid content



$\tau_{0,water+LSF}$ = 1,43 Pa

Viscosity vs. solid content

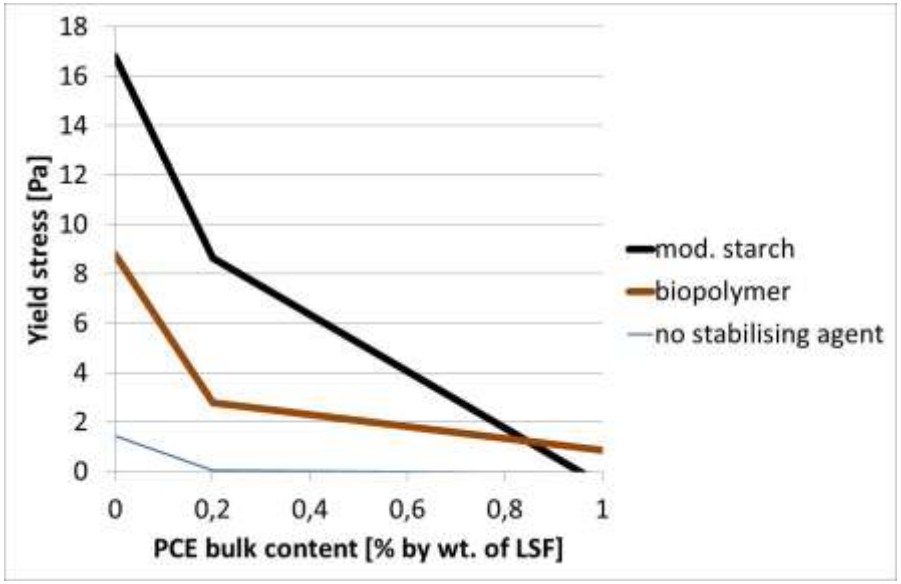


$\eta_{water+LSF}$ = 0,02 Pa s

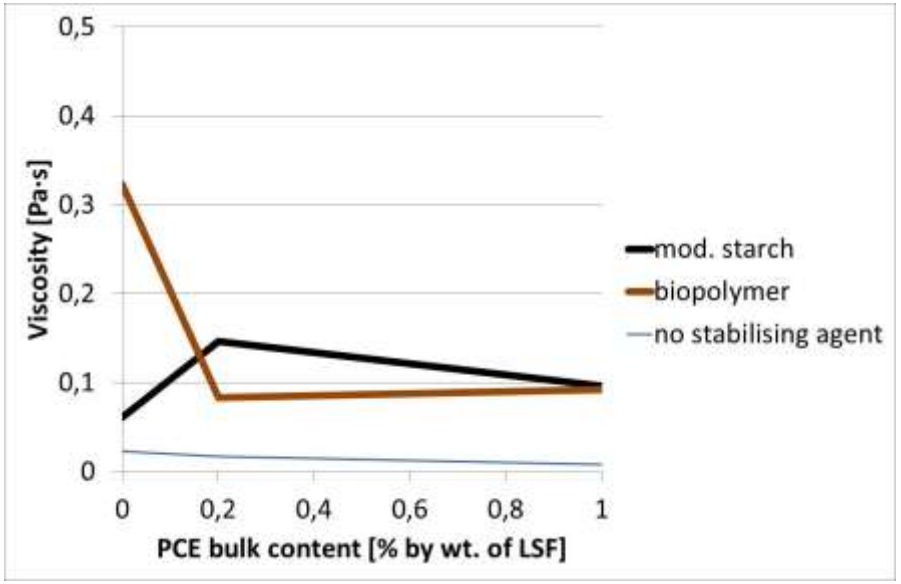
Biopolymer has a strong effect on yield stress already in water. Increasing solid particle content has minor effect on yield stress but high effect on viscosity. While the mod. starch does not affect yield stress in very fluid systems, yield stress increases at higher solid contents. The increase of solid content on viscosity is small.

Influence of the PCE content

Yield stress vs. PCE content, 50% solid vol.



Viscosity vs. PCE content, 50% solid vol.



PCE addition reduces effect of both stabilising agent types significantly.
It seems the biopolymer loses additionally viscosity due to loss of adsorption on particles.

Effects of water binding capacity

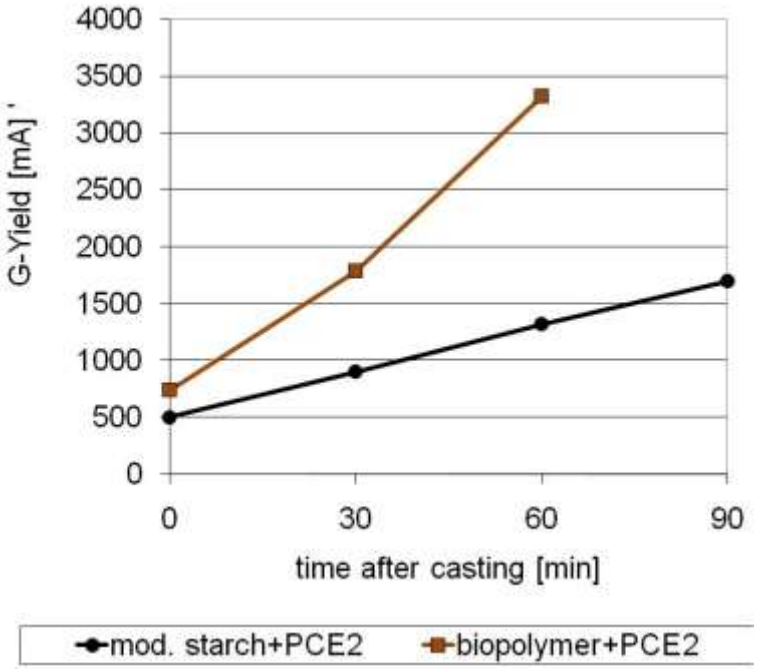
Modified starch at PCE overdose

Biopolymer at PCE overdose

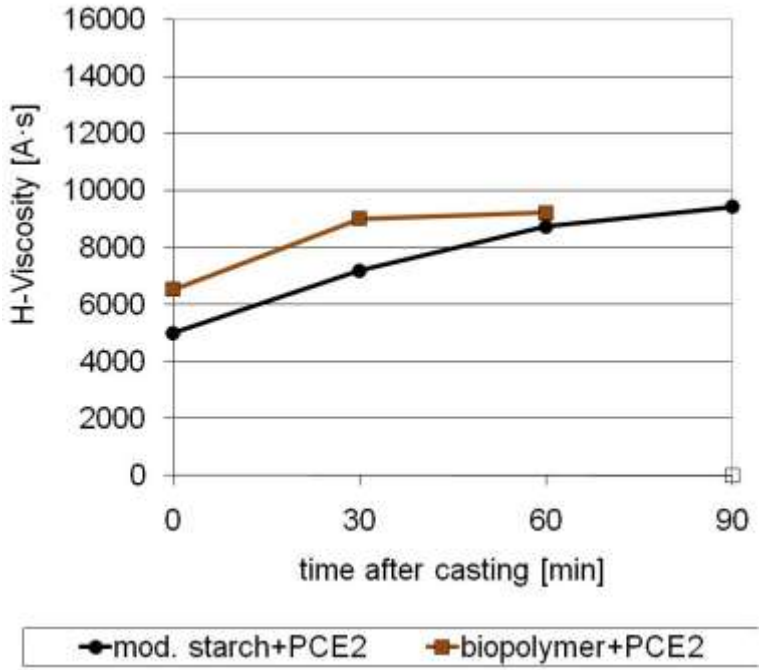
In order to effectively reduce bleeding, a stabilising agent with high water binding capactity is required. The particle stabilising effect of the modified starch cannot avoid segregation of fluid paste.

Influence of stabilising agent on self-compacting concrete

G-Yield (Yield stress)



H-Viscosity



The anionic charge on the biopolymer causes time delayed adsorption on particles, diminishing dispersing effects of PCE, causing quick loss of workability. Particle stabilisation as with mod. starch does not show these effects.

Effects of modifications of one polysaccharide

Background of new investigations:

- **Different stabilising agent types affect rheology and its retention differently due to specific characteristics.**
- **How can characteristics of a single polysaccharide affect rheology with and without PCE?**

Conducted tests

- **Paste tests with limestone filler and different stabilising agents**

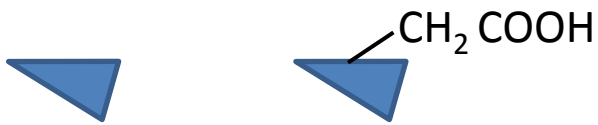
	Water + ST	Low powder content	High powder content	High powder, low PCE cont.	High powder, high PCE cont.
Water	100% by vol.	66,7% by vol.	50% by vol.	50% by vol.	50% by vol
Stabilising agent	0,5% of water	0,5% of water	0,5% of water	0,5% of water	0,5% of water
Limestone filler	-	33,3% by vol.	50% by vol.	50% by vol.	50% by vol.
PCE	-	-	-	0,2% of LSF	1,0% of LSF

Observed polysaccharide modifications

- **Molecule size:**

- **Sulfate content:**

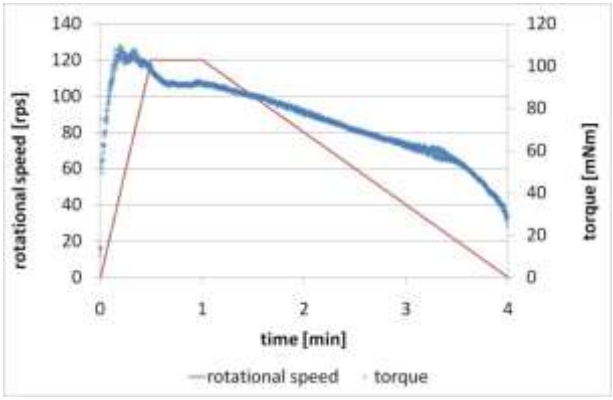
- **Anionic charge:**



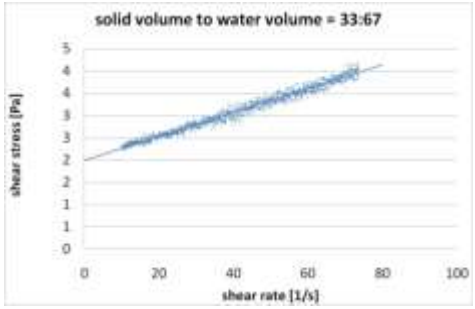
Effects of modifications of one polysaccharide

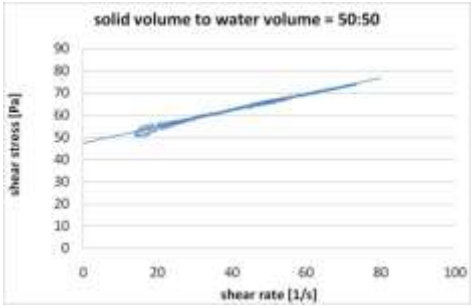
Test specifications

- Basket cell
  (Vogel cell)



- 2 ramps, each 4 minutes

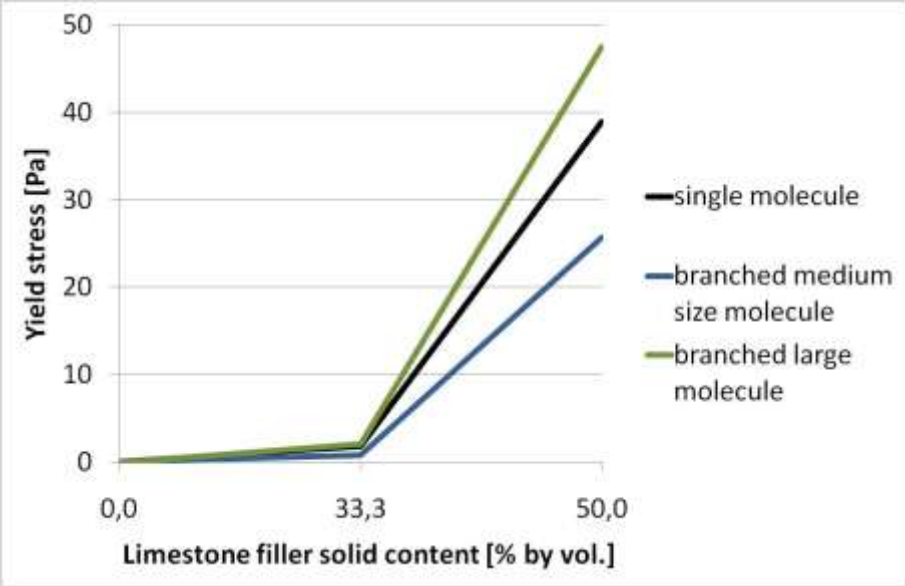


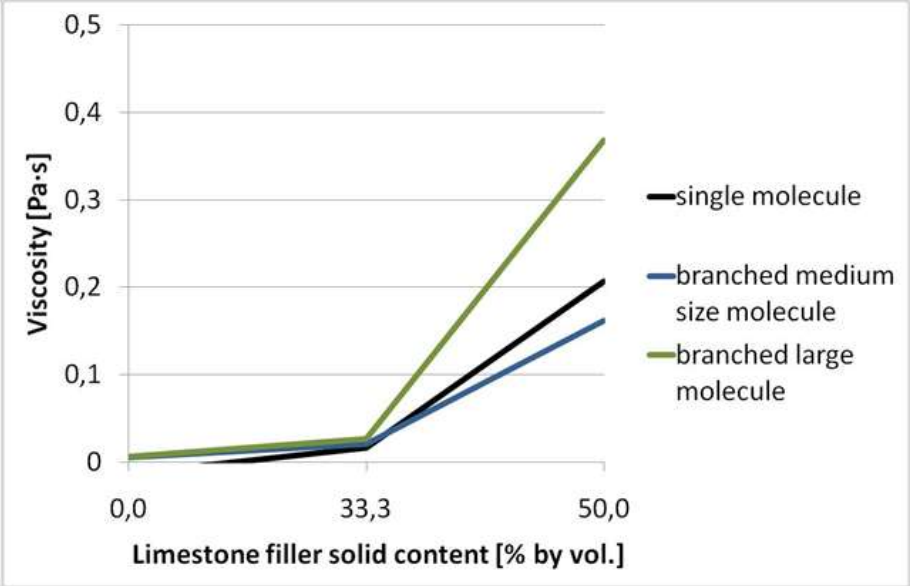


- Bingham approximation

Effects of modifications of one polysaccharide

Influence of the molecule size

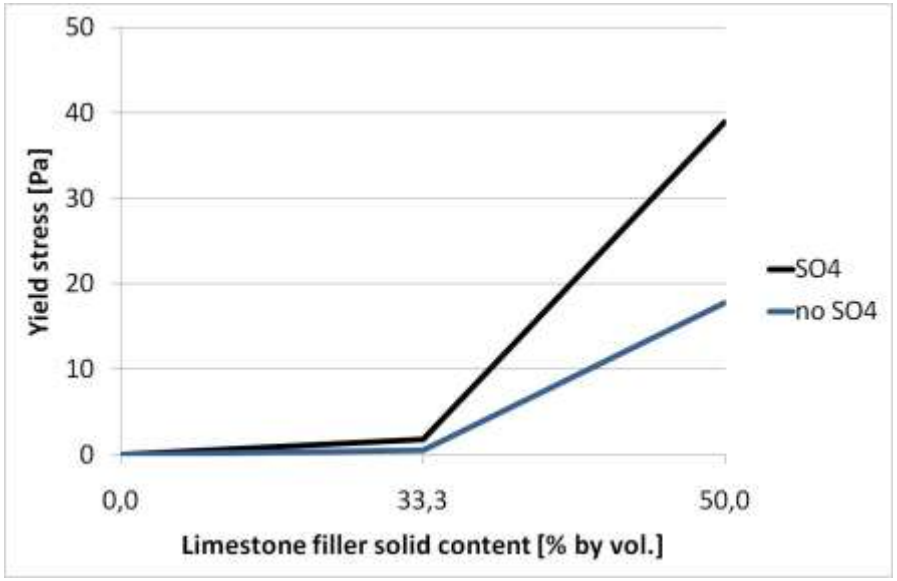


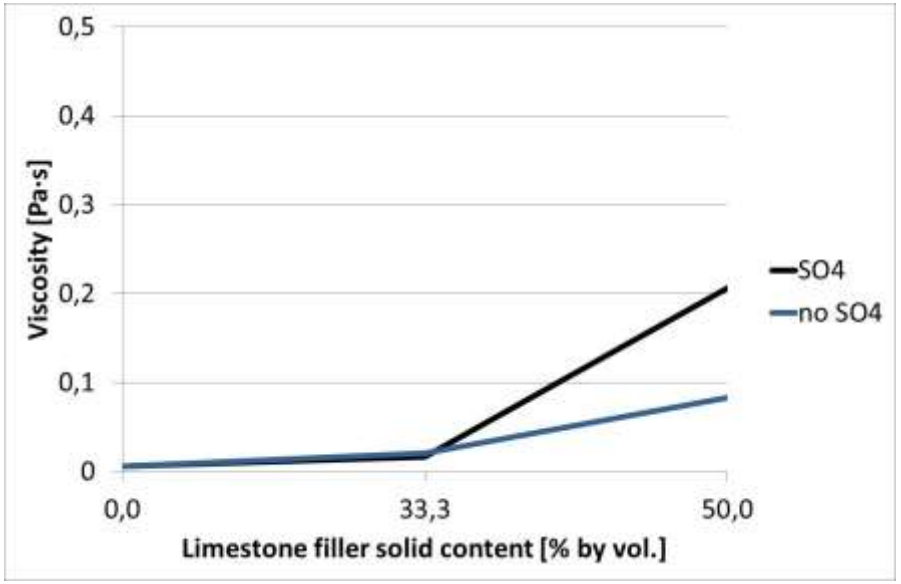


- **The large molecule generates the highest yield stress.**
- **There is no correlation between molecule size and yield stress increase.**

→ **Assumption: Large molecules add component to yield stress and viscosity due to entangling of particles.**

Influence of the sulfate content



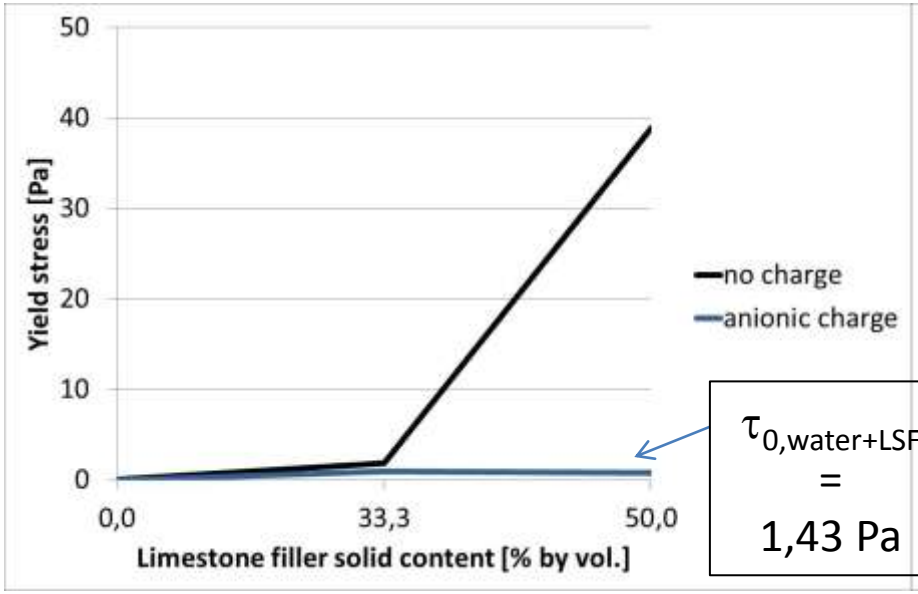


- **The stabilising agent releasing sulfate ions increases yield stress and viscosity more than the agent without sulfate, when solid-to-water ratio increases.**

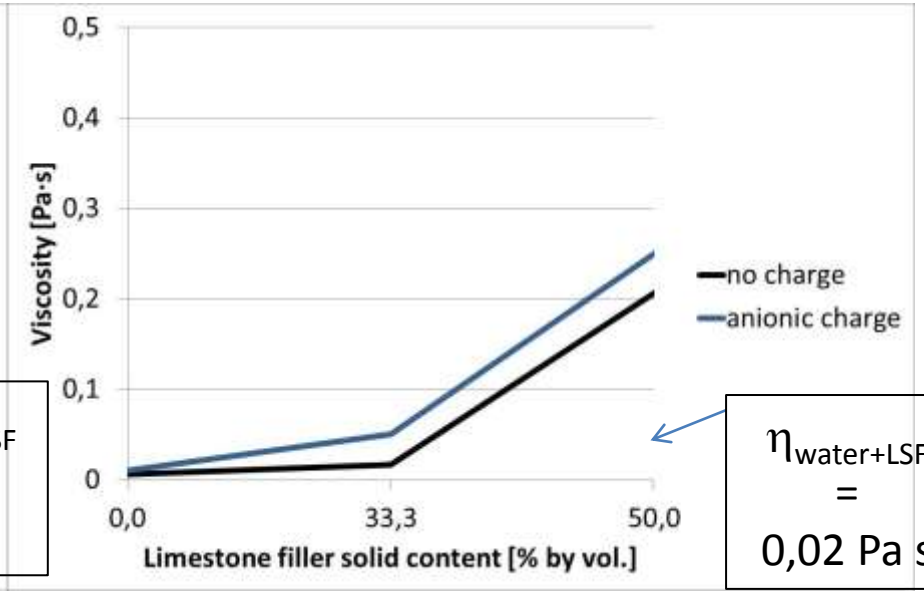
→ **Assumption: Sulfate ions adsorb on limestone filler particles reducing the dispersion forces**

Effects of modifications of one polysaccharide

Influence of the anionic charge



$\tau_{0,water+LSF}$ = 1,43 Pa

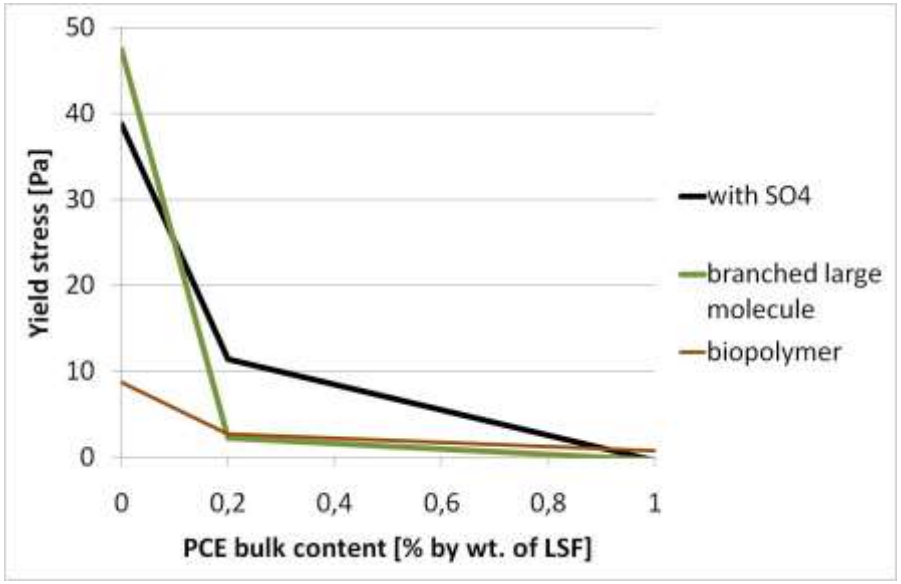


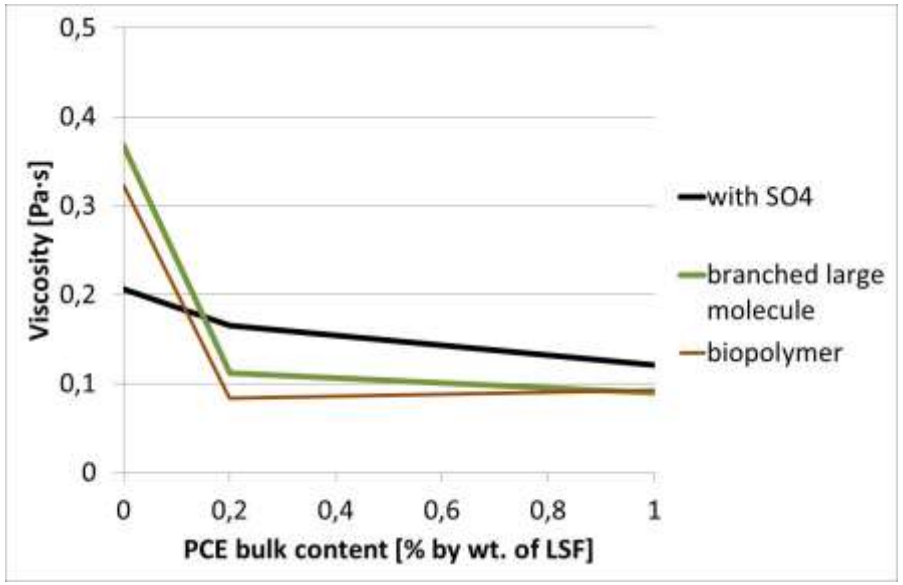
$\eta_{water+LSF}$ = 0,02 Pa s

- **The anionic polymer does not affect yield stress significantly.**
- **At solid-water ratio of 0.5, the measured yield stress with the anionic polymer is in the range of a control mix without stabilising agent.**
- **Viscosity is increased by both stabilising agents without influence of the charge density.**

→ **The polymer with anionic charge really only affects viscosity**

Influence of PCE content on rheology





- **Yield stress drops quickly upon addition of PCE.**
- **The only modification with smaller loss of yield stress is the one with sulfate → adsorption of SO_4 on particles, reduces effectiveness of PCE**
- **Viscosity reduces only moderately with increasing PCE content.**
- **Exception: The long chain mixes lose viscosity significantly at low PCE content but stabilise then.**

Summary

Observation of different agents

- In order to effectively reduce bleeding and segregation in case of „overdose“, highly water immobilising polymers have to be chosen.
- In order to avoid quick loss of performance of SCC, a non adsorbing polymer should be chosen.

Vielen Dank für die Aufmerksamkeit!

Thank you very much for your kind attention!

Modifications of a single polysaccharide

- Modifications of individual parameters in a single polymer can have stong effects, particularly regarding yield stress:
  - Large polymers contribute to increase of yield stress supplementary due to intertwining of particles.
  - PCE has generally no strong effect on viscosity of mixes including stabilising agents.
  - An exception build mixes with large molecules. Here already small amounts of PCE cause a significant drop in viscosity.
  - Modifications that contain sulfate ions have strong effects on yield stress and viscosity. Also in presence of PCE, polysaccharides with SO_4 retain highest yield stress compared to molecules without SO_4.
  - Adding anionic charges to the polymers causes only increase of viscosity without any effect on yield stress.