Clay Tolerant Superplasticizer for Concrete

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Value Proposition

- Opportunity Statement
  - PCE based on a styrene maleic anhydride (SMA) copolymer backbone reduce the sensitivity to clay impurities significantly
- Key benefits of this technology will address the following aspects
  - Intensive washing of aggregates is avoided to lower consumption of clean water
  - Addition of more PCE to compensate for the intercalated quantity will add to cost
  - Retain concrete strength

State of the Art

- Deactivation of PCE in the presence of swellable clays
  - Polyethylene glycol chain get intercalated in montmorillonite layer structure

  S. Ng, J. Plank, "Interaction Mechanism between Na Montmorillonite Clay and MPEG-based Polycarboxylate Superplasticizers", Cement and Concrete Research 42 (2012) 847 – 854

- Possible countermeasures
  - Extensive washing of aggregates
  - Use of scavengers

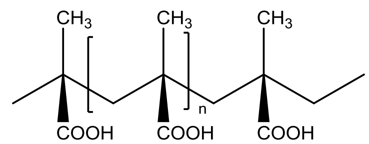
  EP 1838643 B1 describes the use of cationically charged polymers to inert clay impurities

  - Use of superplasticizers without side chains is less effective and does not provide slump retention

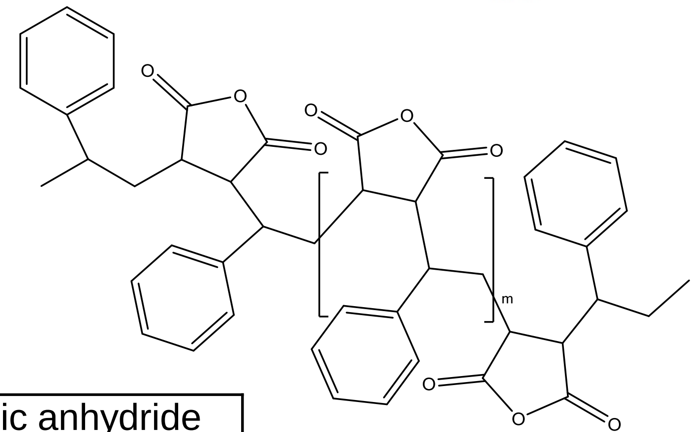
  L. Lei, J. Plank, "A Concept for a Polycarboxylate Superplasticizer Possessing Enhanced Clay Tolerance", Cement and Concrete Research 42 (2012) 1299 – 1306

Structural Elements of PCE

- <u>Backbone Chemistry</u>
  - Polymethacrylic acid
    Mn 3000, Mw 5000

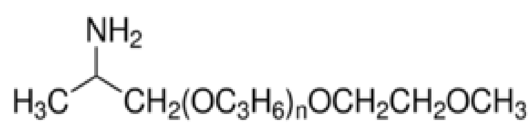


  - Styrene / maleic anhydride copolymer



	Mn	Mw	ratio styrene : maleic anhydride
SMA 1000	2000	5500	1:1
SMA 2000	3000	7500	2:1
SMA 3000	3800	9500	3:1

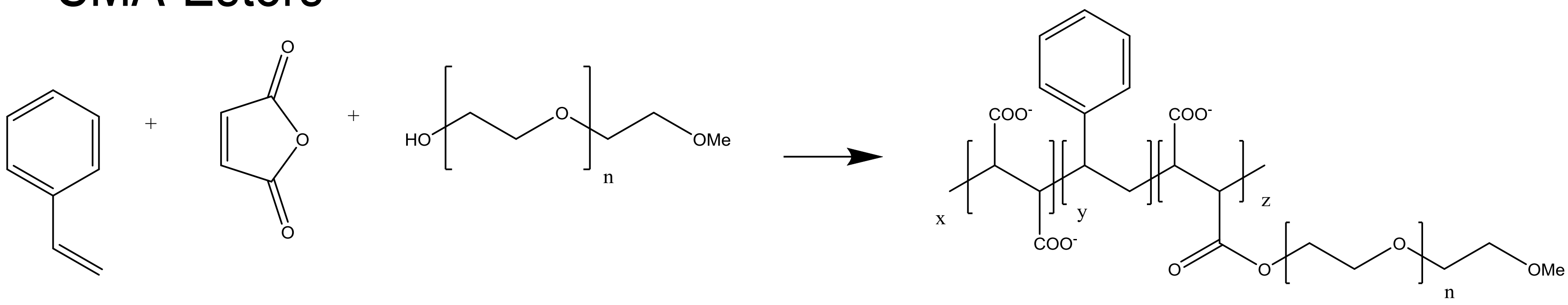
- <u>Sidechain chemistry</u>
  - Polypropylene glycol (NH_2-PPG)
    O-(2-aminopropyl)-O'-(2-methoxyethyl) polypropylene glycol (Mn 600)



  - Polyethylene glycol monomethyl ether
    MPEG 550, 1000, 2000

Superplasticizer Overview

- SMA-Esters



Grafting Ratio is the molar ratio of maleic half ester to maleic acid

- PMAA-Esters
  - Produced using sodium hyperphosphite catalysis
- Commercial PMAA-Ester
- Beta Naphthalene Sulfonate Condensate

Structural Variations

- Backbone Chemistry
  - Acrylic
  - Styrene/Maleic Anhydride – Monomer ratio
- Side Chain Architecture
  - Side Chain Chemistry – EO vs. PO
  - Side Chain Length – 550 to 2000
  - Grafting density

Testing Conditions

MORTAR FORMULATION

Component	(g)
Cement OPC CEM I 42,5 R*	500
Quarzsand H 32	500
Sand particle size 0.2 - 1 mm	600
Sand particle size 1 - 2 mm	400
Superplasticizer (as solid)	1.9
Bentonite clay	8.0
Water	288.1

W/C ratio	0.58
Superplasticizer	0.38% bwc
Clay contamination	0.4% based on solids

We tested for

- Initial flow with/without clay
- Slump retention (1 hour)
- Cement setting retardation

Performance Results

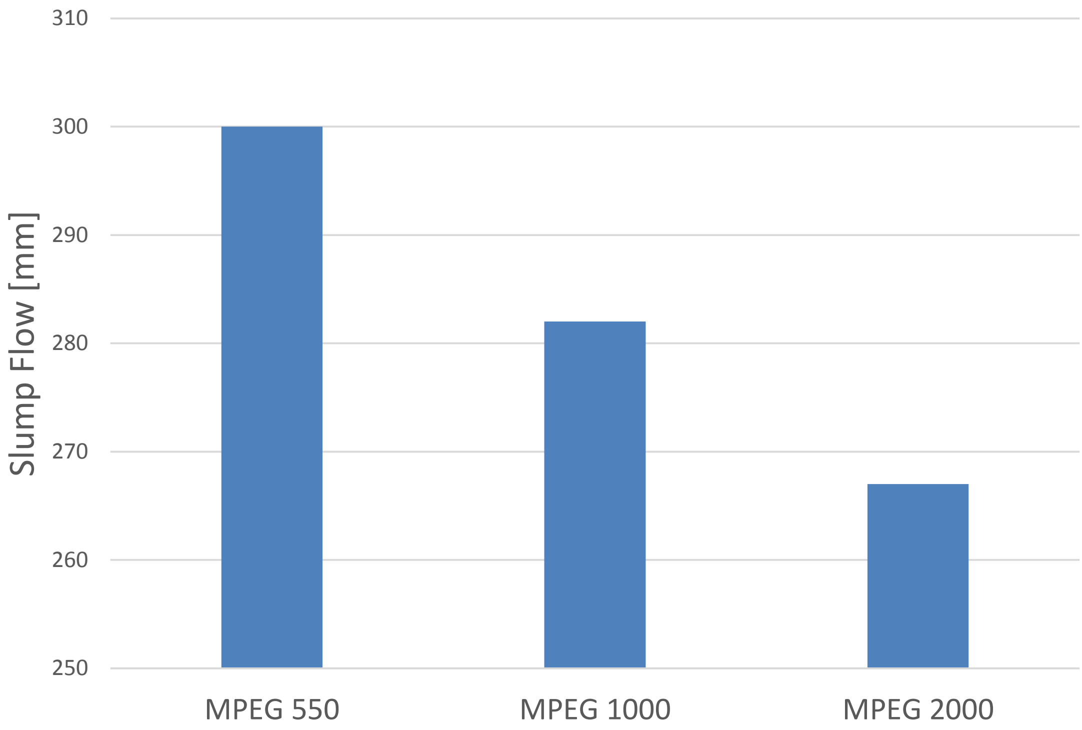
Plasticizer	Backbone	Sidechain	grafting ratio	Slump Value w/o Clay (mm)	Slump Value w/ Clay (mm)	% Difference
Commercial PCE	MAA	MPEG 1000	0.3	300	214	29
Commercial BNS				248	210	15
MPEG-PMAA	MAA	MPEG 550	0.42	277	212	23
NH2-PPG PMAA	MAA	NH2-PPG	0.42	246	229	7
NH2-PPG-SMA A4	SMA 1000	NH2-PPG	0.11	245	222	9
NH2-PPG-SMA A5	SMA 1000	NH2-PPG	0.5	252	234	7
MPEG-SMA A2	SMA 1000	MPEG 550	0.67	300	283	6
MPEG-SMA A3	SMA 1000	MPEG 1000	0.67	282	269	5
MPEG-SMA A5	SMA 1000	MPEG 2000	0.67	267	260	3

The presence of clay causes:

- Strong deactivation of acrylic MPEG PCE
- Strong deactivation of beta naphthalene sulfonate condensate
- Acrylic PPG PCE shows low clay sensitivity, but low plasticizing effect
- SMA based comb polymer with PPG side chain show low clay sensitivity, but low plasticizing effect
- SMA based comb polymer with MPEG side chains show strong plasticizing effect and are clay tolerant
- SMA based comb polymers with MPEG are more effective with shorter side chains

Critical Structural Properties

Side Chain Length

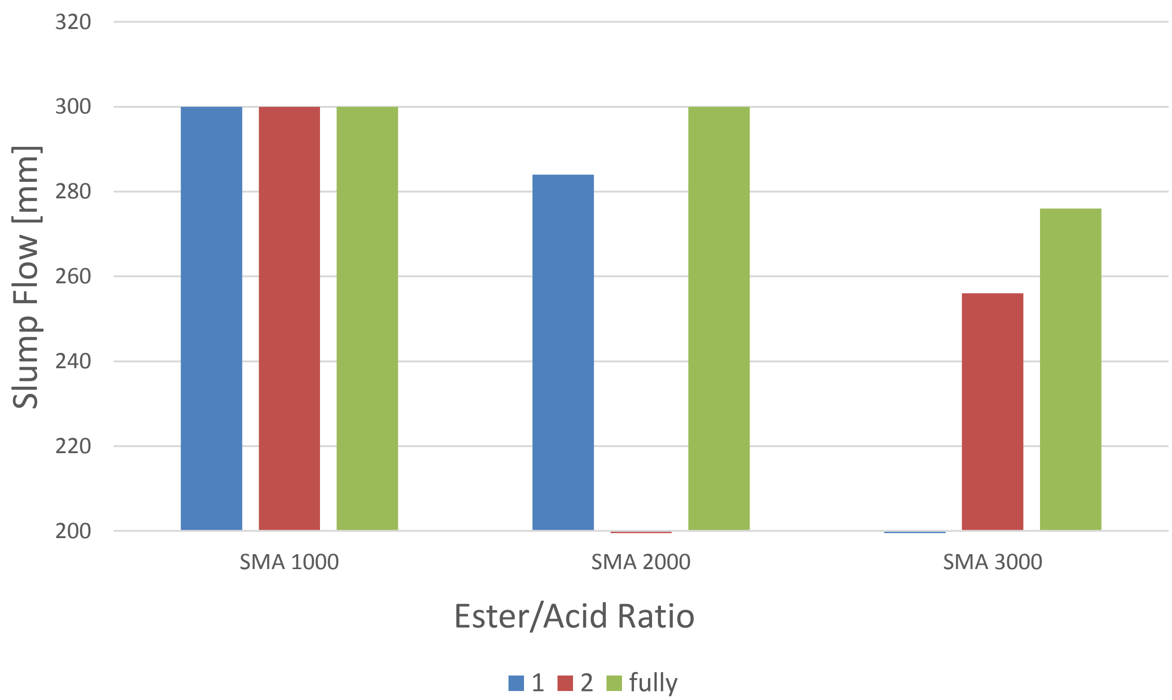


At a given grafting density the shorter side chains perform better

This is contrary to acrylic PCEs

Critical Structural Properties

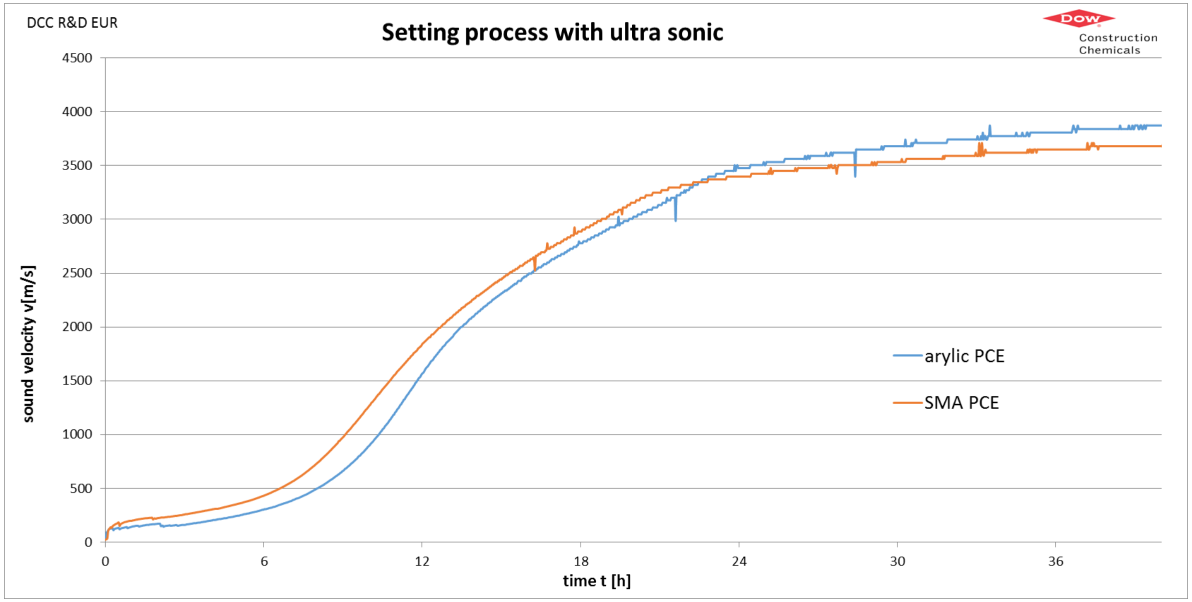
Grafting Density and Backbone Monomer ratio



Best results could be achieved with a backbone of S/MA ratio of 1:1, MPEG 550 and a grafting density of 1 (1:1 ratio of half ester to bi-acid)

Other Properties

- Impact on cement setting rate (without clay)



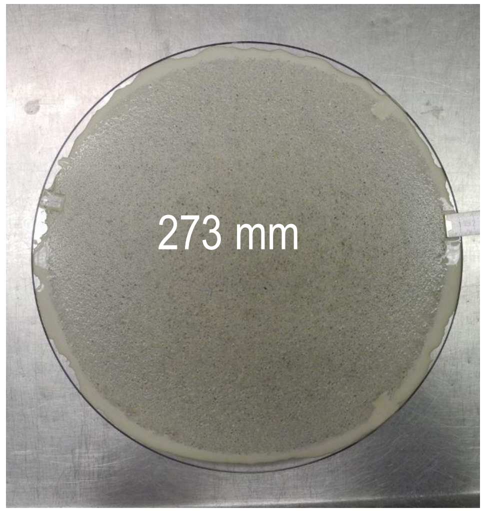
- Impact on concrete strength (without clay)

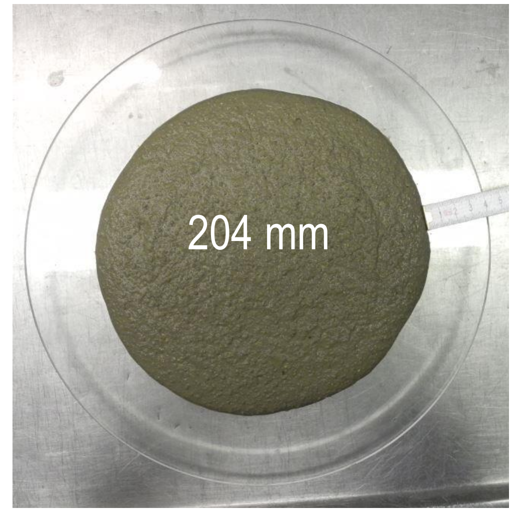
Sample	W/C - Ratio	tensile strength after 1 day (N/mm²)	tensile strength after 7 days (N/mm²)	compressive strength after 1 day (N/mm²)	compressive strength after 7 days (N/mm²)
acrylic PCE	0.50	3.1	5.1	13	29.2
SMA PCE	0.50	3.2	6	13	32.5

Other Properties – Stability

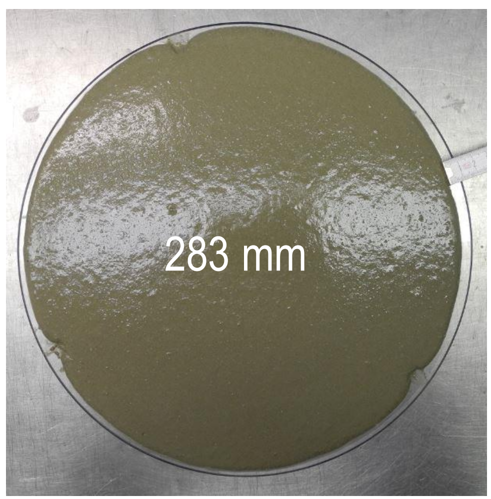
without clay | with clay

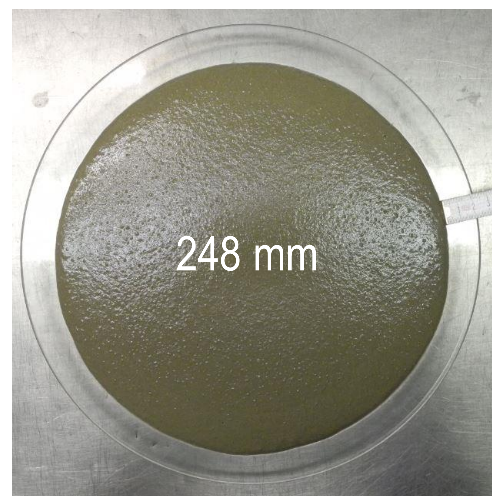
Acrylic PCE
W/C ratio 0.57





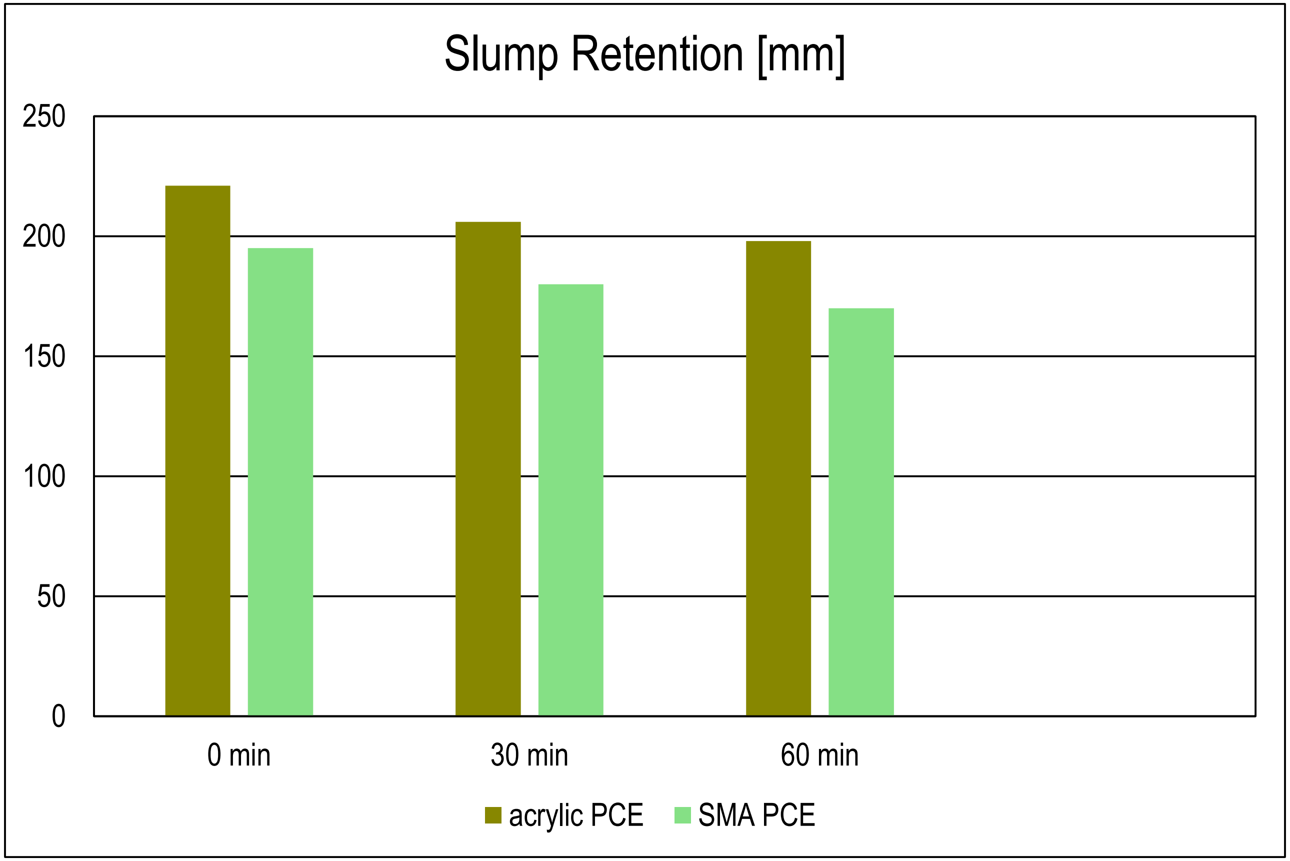
SMA PCE
W/C ratio 0.57





Other Properties – Slump Retention (without clay)

W/C ratio 0.5



Summary

- PCEs with SMA polymer backbone have shown surprising robustness as concrete superplasticizers in the presence of clay
- Their effect on concrete rheology, slump retention, cement setting and strength development is comparable to acrylic PCE
- The bulky, hydrophobic polymer backbone seems to prevent intercalation of the brush polymer
- The dispersion mechanism apparently is different to traditional PCE as low Mw side chains enable improved flow properties
- More work is required to completely understand their mode of action as concrete superplasticizers

Thank you for your attention

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