

Mitigating autogenous shrinkage by means of superabsorbent polymers - effect on concrete properties

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ABSTRACT

(Ultra)-high performance concrete ((U)HPC) is very prone to autogenous shrinkage cracking. These cracks can create preferential pathways for the ingress of harmful substances which can facilitate the corrosion process of the steel reinforcement, resulting in a decreased durability and structural integrity of the concrete structure. Superabsorbent polymers (SAPs) can reduce or even mitigate autogenous shrinkage as they absorb water in the fresh concrete mix and provide it to the cement particles at the right moment in the hydration process, acting as internal curing agent for the concrete. To study the mitigation of autogenous shrinkage by SAPs, five different superabsorbent polymers based on the copolymerization of acrylic acid (AA) with dimethylaminoethyl methacrylate (DMAEMA) were synthesized at Ghent University. This paper focusses on the compatibility tests aiming at evaluating the effect of these SAPs on initial flow and slump life (rheology), hydration kinetics (reactivity) and mechanical properties (3, 7 and 28 days strength). The most promising SAPs will be further studied on their effect to mitigate autogenous shrinkage.

Keywords: superabsorbent polymers (SAPs), cementitious materials, autogenous shrinkage, internal curing, early age properties

1. INTRODUCTION

Superabsorbent polymers (SAPs) are cross-linked, three-dimensional (3D) polymer networks which can retain water from aqueous solutions in huge amounts due to their hydrophilic nature via osmosis. The water retained by SAPs can amount to thousand times their own dry weight¹⁻³. Their hydrophilic nature results from hydrophilic groups incorporated in the polymer structure. SAPs are hydrogels that can swell a lot, which can also demonstrate a reversible behavior by de-swelling. Hydrogels maintain the initial 3D structure of SAPs and cannot dissolve in water basically due to their crosslinking^{4,5}. In literature, SAPs have been described as interesting admixtures for internal curing, self-sealing and self-healing applications in concrete⁶⁻⁹. They can play an important role in the control of the free water balance in the concrete mixture and by that limit autogenous shrinkage cracking. So far, most of the studies on SAP-incorporation in concrete mixtures are focusing on commercially available SAPs that are usually cross-linked copolymers of acrylic acid (AA) and acrylamide (AM) with a given particle size distribution leading to a polycarboxylate molecular structure. However, SAPs can be synthesized with a big variety of hydrophilic side chains (sulfates, sulfonates, phosphates and even quaternary amines) leading to various types of polyelectrolytes. At Ghent University (UGent) SAPs based on the copolymerization of acrylic acid (AA) with dimethylaminoethyl methacrylate (DMAEMA), which leads to an amphoteric molecular structure that is pH-responsive, were synthesized. A first step before implementing the SAPs in (U)HPC concrete mix designs, is to assess the compatibility of the superabsorbent polymers with the concrete as their presence may physically or chemically influence the early age concrete properties. Therefore compatibility tests aiming at evaluating the effect of SAPs on initial flow and slump life (rheology), hydration kinetics (reactivity) and mechanical properties (3, 7 and 28 days strength) were performed. For this, a conventional standard mortar mix was used as reference. Also two commercially available SAPs, of which their use was already reported in literature, were tested and their effect was compared with the synthesized SAPs

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2. MATERIALS AND METHODS

2.1 Synthesis of superabsorbent polymers

The synthesized SAPs were prepared by combining DMAEMA (copolymerized together with AA in the case of poly(acrylic acid-co-dimethylaminoethyl methacrylate) with the bifunctional cross-linker MBA. The redox initiator pair APS and TEMED was added to initiate the polymerization reaction. APS was used at a concentration of 2 w/v% with respect to the total combined weight of the monomers and cross-linker. TEMED was added in a 1/1 vol% ratio with respect to APS. The SAPs were prepared in a three-neck flask under nitrogen atmosphere at 45 °C. After 24 h, the SAP was removed from the flask and purified by incubation in water for 24 h. Then, the SAPs were lyophilized by means of a Christ freeze-dryer alpha 2-4-LSC and ground to a fine powder (d50 approx. 40 µm) with an A11 basic analytical mill.

The following SAPs were synthesized:

- poly (DMAEMA) 4 mol% of MBA cross-linker (100/0)
- poly (AA-co-DMAEMA) 75/25 0.5 mol% MBA cross-linker (75/25 0.5 mol%)
- poly (AA-co-DMAEMA) 75/25 1 mol% MBA cross-linker (75/25 1 mol%)
- poly (AA-co-DMAEMA) 50/50 0.5 mol% MBA cross-linker (50/50 0.5 mol%)
- poly (AA-co-DMAEMA) 50/50 1 mol% MBA cross-linker (50/50 1 mol%)

Next to the five in-house-developed SAPs, two commercially available SAPs were tested as well: Floset 27 cc from SNF FLOERGER with d50 of 40 µm (FLO_40) and SAP A from BASF with d50 of 100 µm (BASF_100).

2.2 Characterization of superabsorbent polymers

The gel fraction of the SAPs was assessed after removing the unreacted particles from the end product via dialysis. The gel fractions were determined by measuring the dry weight of the sample before and after purification using the equation: $G (\%) = W/W_0$ (W = weight of the dry insoluble part of the sample in mg; W_0 = initial dry weight of the sample in mg).

The chemical structure of the SAPs was confirmed using ATR-IR spectroscopy. A PerkinElmer Frontier FT-IR (midIR) combined with a MKII Golden Gate set-up equipped with a diamond crystal from Specac was used.

The filtration test for determining the swelling potential of the SAPs in demineralized water and in cement filtrate were based on the RILEM TC-RSC WG1 recommendation [Schröfl, Snoeck, Mechtcherine, publication in preparation]. In this test, a certain amount of fluid was added to dry SAP particles. After 24 h, the SAP particles definitely reached their equilibrium swelling and the dispersion was filtered using filter paper with particle retention of 12-15 µm. In order to exclude possible absorption of the fluid by the filter paper, the latter was first saturated with the fluid. To minimize evaporation during the test, the test setup was covered with a lid. Swelling capacities in both demineralized water and cement filtrate were determined. The cement filtrate was prepared by mixing 10 g of CEM I 52.5N and 100 ml of demineralized water for 24 h. Afterwards, the slurry was filtered to remove the cement particles and the collected solution was used in the experiments. The experiment was performed at 20°C. After filtering, the amount of fluid that was not absorbed by the SAPs, was recorded. The swelling ratio, i.e. the amount of fluid that can be absorbed by 1 g of SAPs can be calculated by formula (1):

$$\text{Swelling ratio [g fluid/g SAP]} = \frac{W_{\text{fluid added}} - W_{\text{fluid not absorbed}}}{W_{\text{dry SAP}}} \quad (1)$$

With $W_{\text{fluid added}}$ [g]: the amount of fluid before filtration;
 $W_{\text{fluid not absorbed}}$ [g]: the amount of fluid that was not absorbed by the SAPs;
 $W_{\text{dry SAP}}$ [g]: the amount of dry SAPs.

2.3 Mortar composition, mixing procedure and storage

The used mortar mix contained 1350 g of standard sand, 450 g CEM I 52.5N, plasticizer Glenium 51 from BASF with a dosage of 0.25 m% (compared to cement) and 0.5 m% (compared to cement) of SAPs. The obtained W/C ratio was 0.43. In case SAPs were used, additional water was added to compensate for the mixing water uptake by the SAPs. The amount of additional water was kept constant for all the different SAPs, namely at 1.5 times their experimental swelling capacity in cement slurry. The standard mixing procedure was followed:

- 0 – 30 s mixing of water, superplasticizer and cement (speed 140 rpm);
- 30 – 60 s addition of sand while mixing at low speed;
- 60 – 90 s increasing mixing speed to 285 rpm;
- 90 – 120 s scraping the edges of the bowl;
- 120 – 180 s rest;
- 180 – 240 s further mixing (speed 285 rpm).

2.4 Compatibility testing of SAPs in mortar at early age

The initial flow was measured immediately after mixing the mortar on a shocking spread flow table after 15 shocks. Therefore, a truncated cone was placed on the flow table and filled with fresh mortar in two equal layers. Each layer was compacted ten times with a tamping bar and the top layer was struck off at the edge of the cone. Next, the mold was carefully removed in vertical direction and the table was subjected to 15 shocks. Finally, the value of two mutually perpendicular diameters of the mortar spread parallel to the edge of the table was measured to the nearest 10 mm. The average of these two diameters is called the flow. To investigate the flow in time, the sample was remixed every 30 minutes for 30s at a mixing speed of 285 rpm and the same procedure as described above was followed. The measurements were stopped two hours.

To study the influence of SAPs on the mechanical properties, 6 prisms of 40x40x160 mm³ were made. The specimens were stored at a relative humidity of more than 90% and a temperature of 20 ± 2 °C for 48h. At the age of 2 days, the specimens were demolded, wrapped in plastic foil and subsequently stored at standard laboratory conditions (20 ± 2 °C) until the age of testing. After 3, 7 and 28 days, two specimens of each series were subjected to a three-point-bending test in order to obtain the bending strength of the mortar. Subsequently, a compression test was executed on both halves of the broken prisms resulting from the three-point-bending test.

A TAM-AIR isothermal calorimeter was used to study the hydration kinetics of the mixtures under a constant temperature of 20°C. A sample of 14 g mortar was used for this test.

3. RESULTS

3.1 Synthesis and characterization of SAPs

The chemical structure of all synthesized SAPs was investigated by FT-IR (Figure 1). The characteristic bands of both acrylic acid (AA) and DMAEMA could be identified in the corresponding spectra (only results of AA/DMAEMA 50/50 1mol% are shown), which is an indication that the synthesis was successful.

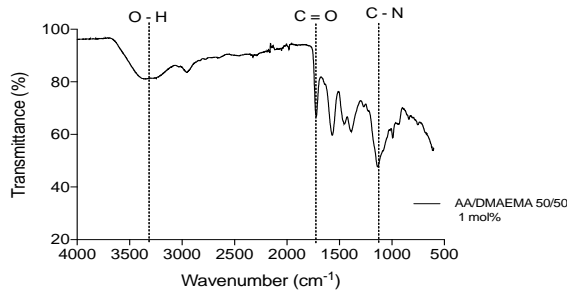


Figure 1: Example of FT-IR analysis of SAP AA/DMAEMA 50/50 1 mol%.

In Table 1, the gel fraction and swelling capacity in both demineralized water and cement filtrate of both the SAPs synthesized at UGent and commercially available SAPs are reported.

Table 1: Gel fraction and swelling capacity of SAPs synthesized at UGent and commercially available SAPs (ND: not determined).

SAP	Gel fraction (%)	Swelling capacity (g/g)	
		Demineralized water	Cement filtrate
DMAEMA 100/0 4 mol%	ND	61.92 ± 1.66	11.29 ± 0.85
AA/DMAEMA 75/25 1 mol%	98.9 ± 0.5	10.34 ± 2.07	13.61 ± 0.59
AA/DMAEMA 75/25 0.5 mol%	98.7 ± 0.9	10.72 ± 3.25	16.58 ± 0.16
AA/DMAEMA 50/50 1 mol%	98.9 ± 0.5	26.67 ± 3.70	19.31 ± 1.03
AA/DMAEMA 50/50 0.5 mol%	ND	54.74 ± 1.88	23.81 ± 0.19
FLO_40	ND	262.21 ± 5.45	21.15 ± 1.60
BASF_100	ND	250.99 ± 5.45	22.30 ± 2.25

It can be seen from Table 1 that the developed SAPs have high gel fractions (%), meaning that the synthesis was successful. The swelling results showed that increasing the amount of DMAEMA in the SAPs, results in a higher swelling capacity. As anticipated, a lower concentration of MBA also resulted in a higher swelling capacity. When comparing the swelling in demineralized water (pH 7) and in cement filtrate (pH 12), it can be seen that in case of AA/DMAEMA 75/25 for both 0.5 mol% and 1 mol% MBA concentrations, in contrast with general expectations, the swelling capacity in demineralized water is somewhat lower than in cement filtrate due to the pH responsive behavior of this type of SAPs. When comparing the swelling behavior of the synthesized SAPs with the behavior of commercial SAPs, it can be seen that the commercial SAPs swell much more in demineralized water compared to synthesized SAPs. In case of swelling in cement filtrate, this difference becomes much more limited.

3.2 Influence of SAPs on the early age characteristics of mortar

Figure 2Error! Reference source not found. illustrates the initial slump of the reference mixture as well as the slump of the mixtures containing SAPs that were synthesized at UGent and containing the two commercial SAPs. The reference mixture reaches a slump of 20.5 cm, whereas the slump of the mixtures containing UGent SAPs have a varying initial slump from 15 cm to 18.5 cm. In case of commercially available SAPs, the addition of SAPs leads to a decrease in initial slump compared to the reference mixture. The initial slump is 13.25 cm and 11 cm for mixtures with the SAPs from FLOERGER and BASF, respectively.

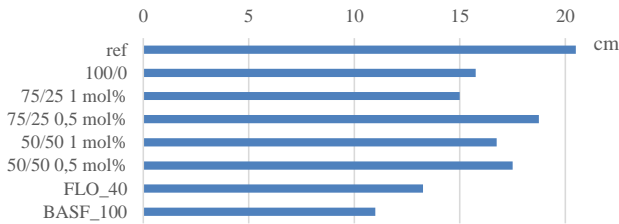


Figure 2: Initial flow of the different mortar mixtures, 0.5 m% SAP compared to cement.

The flow remains relatively constant in time in most of the cases (see Figure 3). In fact, the reference mixture without SAPs shows one of the largest losses in flow as it goes from an initial value of 20.5 cm to a value of 16.75 cm after 120 min.

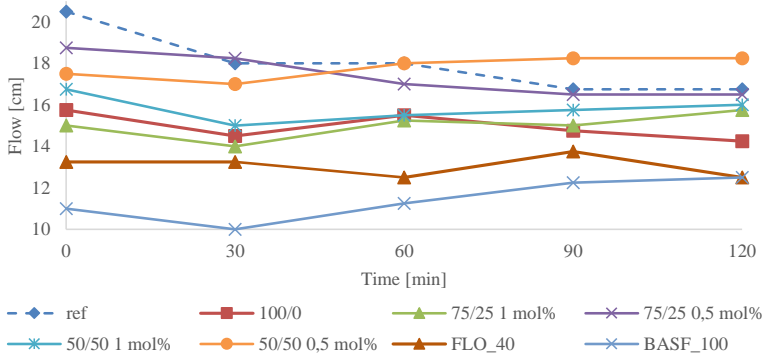


Figure 3: Flow in time, measurements every 30 minutes after 30 s of remixing.

Table 2 and Table 3 summarize the results from the three-point-bending test and the compression test, respectively. The mixtures with the 100% DMAEMA SAP and the 75/25 1 mol% SAP look very promising as they show a compressive strength reduction of only around 10% and 15% after 7 days, compared to the reference. After 28 days, the compressive

strength loss is even less, namely 4% and 6%, which is much better than the results obtained for the commercially available SAPs.

Table 2: Summary of bending strength after 3,7 and 28 days.

Naam	Bending strength [N/mm ²]								
	day 3			day 7			day 28		
	mean	st.dev	strength compared to ref [%]	mean	st.dev	strength compared to ref [%]	mean	st.dev	strength compared to ref [%]
ref	7.50	0.59	/	8.44	0.09	/	9.49	0.46	/
100/0 4 mol %	7.03	0.41	-6.27	7.09	0.1	-16.00	9.17	0.44	-3.37
75/25 1 mol%	6.73	0.42	-10.27	6,68	0.3	-20.85	7.29	0.06	-23.18
75/25 0.5 mol%	6.33	0.44	-15.60	7.27	0.01	-13.86	7.02	0.11	-26.03
50/50 1 mol%	6.12	0.21	-18.40	5.66	0.33	-32.94	6.78	0.07	-28.56
50/50 0.5 mol%	5.96	0.15	-20.53	5.37	0.12	-36.37	6.00	0.15	-36.78
FLO_40	5.57	0.18	-25.73	6.47	0.32	-23.34	6.45	0.25	-32.03
BASF_100	5.75	0.16	-23.40	6.49	0.13	-23.10	7.07	0.02	-25.50

Table 3: Summary of compressive strength after 3, 7 and 28 days.

Naam	Compressive strength [N/mm ²]								
	day 3			day 7			day 28		
	mean	st.dev	strength compared to ref [%]	mean	st.dev	strength compared to ref [%]	mean	st.dev	strength compared to ref [%]
ref	53.03	2.35	/	63.94	0.71	/	68.35	6.7	/
100/0 4mol%	45.76	0.85	-13.71	57.41	0.75	-10.21	65.38	1.94	-4.35
75/25 1 mol%	41.79	0.45	-21.20	53.90	1.27	-15.70	63.86	1.11	-6.57
75/25 0,5 mol%	36.05	2.87	-32.02	48.66	2.45	-23.90	57.71	1.64	-15.57
50/50 1 mol%	33.89	0.37	-36.09	44.10	1.04	-31.03	50.83	1.94	-25.63
50/50 0,5 mol%	26.61	1.07	-49.82	35.05	0.81	-45.18	43.20	0.74	-36.80
FLO_40	32.82	0.14	-38.11	41.44	0.64	-35.19	50.55	0.86	-26.04
BASF_100	32.31	1.73	-39.07	40.97	3.18	-35.92	49.58	3.04	-27.46

Figure 4 shows the heat production rate as a function of time. It can be seen that the hydration of the mixtures containing SAPs is slightly retarded compared to the reference mixture as indicated by the small shift to the right and the reduction in maximum heat flow values.

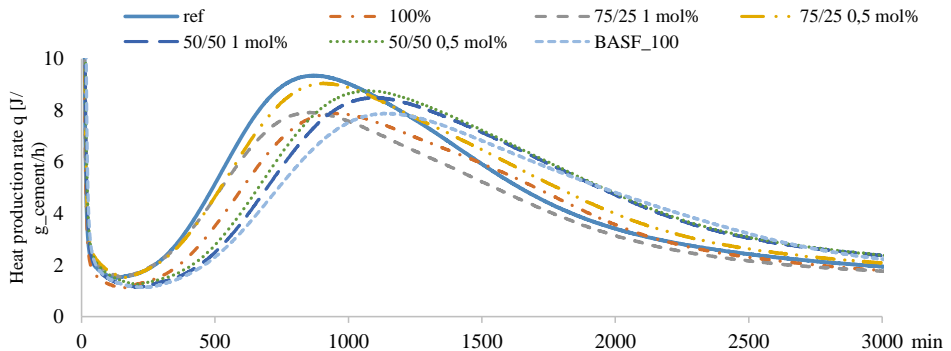


Figure 4: Heat production rate as a function of time.

4. CONCLUSIONS

The following conclusions can be drawn based on the results of this study where SAPs are added to mortar to study the effect on the early-age properties:

When SAPs are added to the mix, the initial slump is somewhat lower than for the reference mixture, even when additional water is added to compensate for the water uptake as measured by filtration tests in cement slurry. Further research should focus on finding the ideal amount of additional water, so no difference in workability is seen between the reference and the SAP-containing mixtures. However, SAP-containing mixtures are able to keep their slump quite constant during the first hours, whereas the reference mixture shows a slight loss of slump over time.

In case of the 100% DMAEMA SAP and the 75/25 1 mol% SAP the influence on the compressive strength is limited: these SAPs show only a strength reduction around 10% and 15%, respectively after 7 days compared to the reference mixture. After 28 days, the compressive strength reduction is even less: only 4% and 6% respectively. Mixtures with the tested commercial SAPs showed a much higher strength decrease of around 38% and 35% after 3 d and 7 d, respectively. It should be noted that if only internal curing of concrete is envisaged as a self-responsive property, the current dosage of 0.5 m% SAP by weight of cement may be reduced, so in that case an even more limited effect on strength is expected.

The addition of SAPs leads to a limited retardation in the hydration of the mixtures as well as to a reduction in maximum heat flow values observed in an isothermal calorimeter.

The optimization of the synthesized SAP and the optimum amount of cross-linker will be the focus of further research. In addition, the influence of different particle sizes and amounts will be studied more thoroughly. In a next step, the synthesized SAPs will be incorporated in mortar and (U)HPC and their influence on mitigating autogenous shrinkage will be studied by corrugated tube tests according to ASTM C 1698 – 09 and ring tests according to ASTM C 1581 – 04.

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