

# The development of SAPs for reducing autogenous shrinkage and accomplishing self-healing and self-sealing properties in concrete

Els Mannekens<sup>1</sup>, Geert Deroover<sup>1</sup>

<sup>1</sup> ChemStream bvba, Drie Eikenstraat 661, 2650 Edegem, Belgium – email: [els.mannekens@chemstream.be](mailto:els.mannekens@chemstream.be); [geert.deroover@chemstream.be](mailto:geert.deroover@chemstream.be)

## Abstract

Super absorbing polymers (SAPs) are widely studied in concrete as additives to mitigate autogenous shrinkage and to add self-healing and self-sealing properties to the concrete. [1]

When buying commercial SAPs, one is usually stuck to a specific SAP chemistry, to defined particle sizes and in many cases to huge swelling degrees of the SAP particles. We think however that different parameters like the type of chemistry, the crosslinking degree or the swelling potential and the particle size of the SAP powders are crucial for optimizing the SAP-admixture for each type of concrete. ChemStream performed the bulk synthesis of a specific type of SAP that was crosslinked in different degrees and that was further dried and grinded to a variety of particle sizes in order to be tested in concrete.

Keywords: super absorbing polymer, bulk polymerization, crosslinking, particle size distribution, concrete additive

## 1. Introduction

Commercial available SAPs are usually powders containing a specific chemistry, particle size distribution (PSD) and swelling capacity in water. Most of the commercial SAPs are built from the monomers acrylic acid (AA), partially neutralized to its salt or carboxylate form ( $-\text{COO}^-\text{M}^+$ ), and acrylamide (AAm).[2] They are only slightly crosslinked in order to have huge swelling properties up to 300-400 g demineralized water / g SAP, because they are produced to be used in sanitary and convenience products. When these commercial SAPs are tested as additives in concrete mixes, it is hard to relate the results to the effect of the chemistry, to the influence of the particle size or to the crosslinking degree or swelling capacity of these products.

In the LORCENIS project we wanted to understand better which SAP parameters are influencing which concrete characteristics. Therefore, ChemStream synthesized a variation of SAPs, based on a different type of chemistry, having various crosslinking degrees (and thus water swelling capacities) and grinded them to different particle size distributions ranging from 20 to 500  $\mu\text{m}$  in diameter.

At ChemStream experience was built up in the past on the formulation of UV-curable hydrogel formulations that deliver a water-absorbing coating after application on a substrate and subsequent curing by UV-light.[3] The chemistry used in this application is not based on carboxylate chemistry as mentioned above, but on sulfonate chemistry. Sulfonic acids are much stronger acids than carboxylic acids and they lead to much higher osmotic forces for attracting the water into the formed hydrogel networks. Additionally they are less influenced by changes in the pH of their environment.

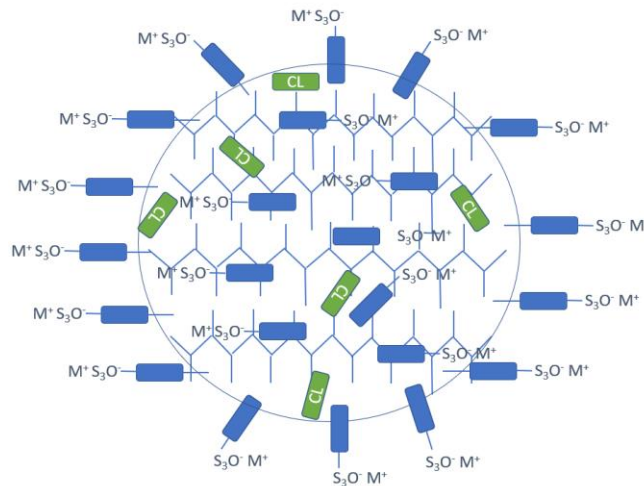


Figure 1: Schematic representation of a SAP particle containing a dense network of sulfonate groups and some crosslinks (green)

## 2. Materials and methods

A bulk polymerization reaction was developed at ChemStream using concentrated aqueous solutions of sodium vinyl sulfonate (SVS) and 2-acryloylamino-2-methylpropane-1-sulfonate (NaAMPS) as monomers, N,N'-methylene bisacrylamide (MBA) as crosslinker and potassium persulfate (KPS) as thermal initiator. The reagents were added together in a 3-necked flask, stirred under nitrogen, and gradually heated up to 70°C. At about 60°C the exothermic reaction started and led to a fast thickening of the reaction mixtures (gelation) thereby stopping the stirring process. During gelation, the temperature rose to about 100°C and the gels were further left to cool down before cutting them into smaller pieces and drying them in an oven at 80°C for removal of the rest water. The method was finetuned in order to make SAP batches up to 3 Kg in size.

The dry SAP pieces were then grinded in a RETSCH centrifugal mill ZM200 in order to obtain powders with a defined particle size distribution (PSD).



Figure 2: Pictures of the 15 L reactor at ChemStream for making SAPs and the RETSCH ultra centrifugal mill ZM200 for grinding the SAPs to powders

The synthesized SAPs were further checked for their swelling potential in demineralized water (g DW/g), for their swelling potential in cement filtrate (g CF/g), for their percentage of the water soluble (not cross-linked) fraction after synthesis (% solubles), and for their particle size distribution (PSD).

The filtration tests for determining the swelling potential of the SAPs in DW (g DW/g) and in CF (g CF/g) were based on the RILEM TC-RSC WG1 recommendation.[4]

In order to determine the % of the soluble and thus not-crosslinked polymer fraction, the water swollen hydrogel (in DW) was filtered from the excess of water after swelling to its maximum swollen state and was then dried again in an oven of 80°C. The weight loss was measured between the dried SAP after swelling ( $M_1$ ) and the initial dry SAP before starting the swelling procedure ( $M_0$ ). The % solubles was then calculated as follows:

$$\% \text{ Solubles} = \frac{(M_0 - M_1)}{M_0} \times 100 \quad (2)$$

The PSD of the grinded SAP powders was determined using a Malvern Mastersizer 2000 instrument that measures the size distribution of particles in the wet state (in ethyl acetate) by laser diffraction. The medium value of the PSD  $D_{50}$  is represented in  $\mu\text{m}$ .

### 3. Results and discussion

Firstly, we checked the swelling behavior of different [SVS-co-NaAMPS] SAPs that were prepared by only varying the amount of crosslinker MBA. (Each of these samples had a mean particle size  $D_{50}$  of 40  $\mu\text{m}$ .)

From the graph in Figure 3 it is very obvious that the more crosslinker is used the less fluid is taken up by the SAPs. Indeed, since the polymer networks are more tightly linked their structure is less open to absorb big amounts of fluids. It is also very clear that DW is absorbed in much bigger amounts than the CF. This is very logical since the CF contains many salts that lower the difference in osmotic pressure and thus lower the sucking force from the SAP-network. The  $\text{Ca}^{2+}$  ions that are present in the CF can even act like extra non-covalent crosslinkers, since they can coordinate with 2 different sulfonate ions from the polymer network, thus creating extra crosslinks.

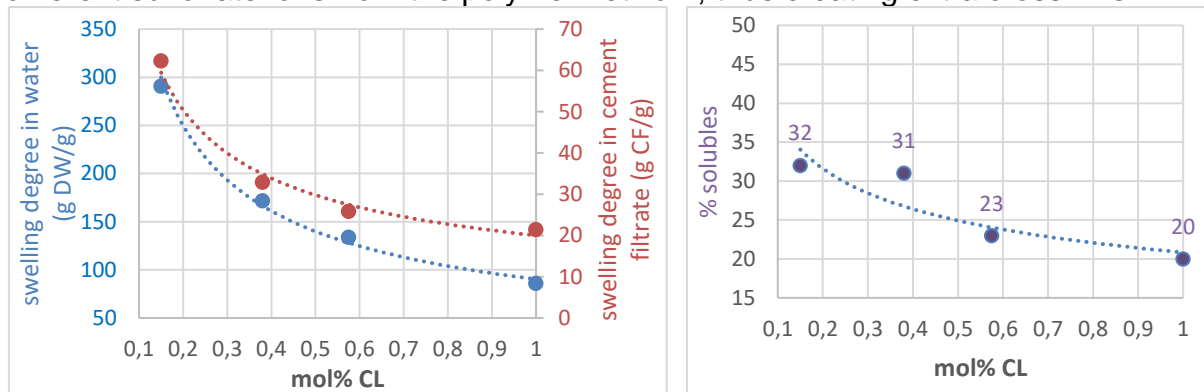


Figure 3: The swelling characteristics in DW and in CF and the % of solubles of different [SVS-co-NaAMPS]SAPs (with  $D_{50} = 40 \mu\text{m}$ ) having different crosslinking degrees

Secondly, for the same set of SAPs the water soluble fraction after synthesis was also measured. This fraction contains non-reacted monomers and linear oligomers that are not crosslinked within the SAP network, which is typical for fast bulk polymerization reactions. We see a trend that the more crosslinker is used, the less free solubles are present in the final SAP network. This makes perfectly sense since more crosslinker can fixate more material within the polymer network.

Thirdly, in order to check the range of particle sizes that were possible to obtain using the RETSCH ultra centrifugal mill ZM200, the above mentioned SAPs were milled

using a variation of parameter settings of the RETSCH (sieve mesh size (mm) and centrifugal speed (rpm)) and the PSD's of the obtained powders were measured using the Malvern Mastersizer 2000 as explained in part 2.

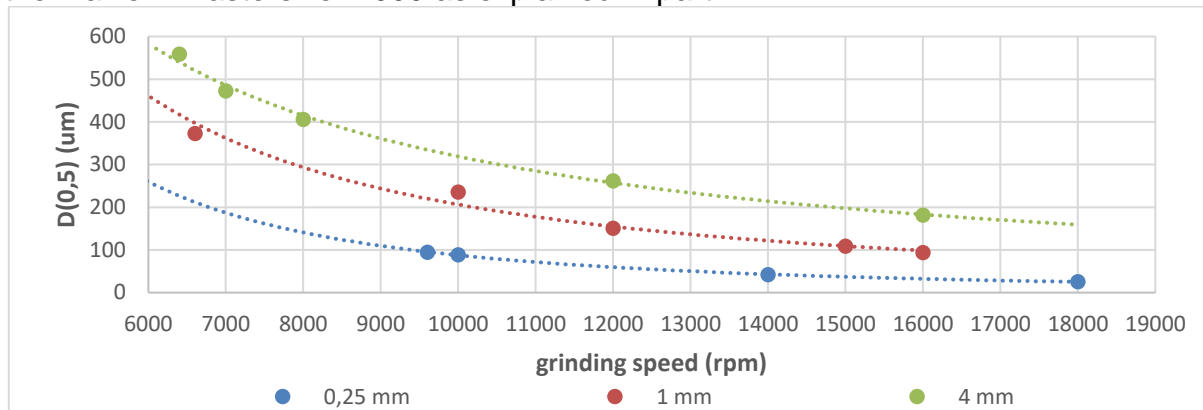


Figure 4: Mean PSD's ( $D_{50}$  in  $\mu\text{m}$ ) for the milling of SAPs using sieves with different mesh sizes (0.25, 1 and 4 mm) at different centrifugal speeds (rpm) of the RETSCH ZM200 system.

It is clear from the graph that PSD's of SAP powders can be obtained from 10-20  $\mu\text{m}$  to about 600  $\mu\text{m}$ . The bigger the mesh size of the sieve, the broader the size distribution of the particles. The grinding process does not seem to alter the swelling properties of the SAPs in DW or CF, nor the amount of water soluble fraction in the SAPs.

#### 4. Conclusion

ChemStream developed a straightforward bulk synthesis to prepare a range of [SVS-co-NaAMPS]SAPs up to 3 Kg scale with varying crosslinking degrees and thus swelling properties. The high hardness of these SAPs gave us the opportunity to use the RETSCH ultra centrifugal mill ZM200 for grinding them into powders of varying sizes ( $D_{50}$  of 10-20  $\mu\text{m}$  up to 600  $\mu\text{m}$ ). The SAPs were finally prepared with 4 different crosslinking degrees (0.15, 0.38, 0.58 and 1 mol% of MBA) of which each was grinded into 3 different PSD's ( $D_{50} = 40 \mu\text{m}$ ,  $100 \mu\text{m}$  and  $500 \mu\text{m}$ ) and subsequently provided to the LORCENIS partners to be tested as additives in cement and concrete systems.

#### Acknowledgements

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