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BIO-BASED PH-RESPONSIVE SUPERABSORBENT POLYMERS FOR SELF-HEALING CRACKS IN CONCRETE

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Abstract
Cracks endanger the durability of concrete. Introducing a superabsorbent polymer (SAP) during concrete mixing can create a self-sealing and -healing construction. SAPs are able to take up aqueous solutions up to several hundred times their own weight. Bio-based SAPs starting from polysaccharides have gained increasing interest in recent years due to their biocompatibility, non-toxicity and low price. The use of pH-responsive SAPs can also be extremely useful as they should only swell more upon crack formation and less during mixing of the SAPs in the concrete. The present work describes the development and the characterization of SAPs based on methacrylated polysaccharides (alginate and chitosan) combined with pH-responsive monomers dimethylaminoethyl methacrylate (DMAEMA) and dimethylaminopropyl methacrylamide (DMAPMA). The materials exhibited a high moisture uptake capacity up to 120% of their original weight with a negligible hysteresis. The pH-responsive swelling behavior was studied in aqueous and cement filtrate solutions with a varying pH. Chitosan combined with DMAEMA or DMAPMA showed the targeted pH-responsive swelling. Chitosan combined with DMAPMA also showed a limited compression strength reduction and a promising self-sealing and -healing behavior and could thus be considered as a very interesting future solution to seal and heal cracks in concrete.

1. Introduction

Concrete is nowadays still the most important building material, mostly due to its ease of use, good mechanical and durability properties and especially due to its relatively low cost compared to other construction materials. Annually, over 10 billion tons are produced [1]. However, it has a low tensile strength. Therefore, concrete is nearly always reinforced with steel bars. This low tensile strength can lead to crack formation, which is one of the most destructive problems in concrete applications as these cracks can endanger the durability of concrete. This can lead to corrosion of the reinforcement, since a pathway for harmful

particles dissolved in fluids and gases is generated [2]. Repairing of cracks often is performed with external techniques such as manual repair with epoxy [3], polyurethane [4], etc. The maintenance and repair with external techniques is often expensive, time-consuming and visually unattractive. These costs can even exceed half of the annual construction budget [5]. Therefore, efforts have been made by researchers to develop concrete that automatically seals and heals any cracks that may form. Standard concrete already possesses the ability to heal small cracks by deposition of calcium carbonate in a process called autogenous healing [6, 7]. Addition of superabsorbent polymers (SAPs) is a possibility to simulate the self-healing of concrete. SAPs are cross-linked polymer networks which can swell up to several hundred times their own weight in aqueous solutions. Previous work has already been performed in our research group regarding synthetic SAPs based on acrylic acid and acrylamide for self-sealing and -healing applications in concrete [8, 9]. These materials were already quite interesting for the intended application. However, they showed a severe effect on the strength upon incorporation. When these SAPs were mixed in mortar, they take up some of the added water which can subsequently be released inside the mortar during the hardening process. This leads to a higher degree of hydration and a more gradual drying, increasing the strength of the concrete and reducing the chance of cracks to manifest. However, as the SAP releases its water, it shrinks and leaves behind pores in the matrix which negatively influence the compressive strength. Which effect contributes the most depends on the water/cement ratio [10, 11]. For self-healing applications, high SAP amounts are required (up to 1% relative to cement mass). Therefore, the macropore formation becomes more critical especially when high amounts of additional water are used to compensate for the loss in workability. To minimize this effect, pH-responsive basic monomers were used here to control the swelling in such a way that the formed SAPs will almost not swell at a high pH (the pH of fresh mortar is 12.5-13), but when a crack occurs and water enters, they will swell more and do their job. In other previous work from the author, alginate biopolymers have been indicated as a high-potential and low-cost polymer for sustainable concrete repair [12]. Natural polysaccharides have the advantage of being renewable, environment-friendly and have a low cost. The current work will therefore report on the development, characterization and investigation of the self-healing potential of SAPs based on methacrylated polysaccharides combined with basic monomers.

2. Materials and methods

2.1 Materials

Sodium alginate and chitosan (used polysaccharides), methacrylic anhydride (MAAH, used for modification of the polysaccharide), sodium hydroxide (NaOH, used for creating aqueous solutions with varying pH-values), hydrochloric acid (HCl, used for creating aqueous solutions with varying pH-values), acetic acid (used to dissolve chitosan), dimethylaminoethyl methacrylate (DMAEMA, used monomer), dimethylaminopropyl methacrylamide (DMAPMA, used monomer) and ammonium persulfate (APS, used initiator for polymerization) were purchased from Sigma-Aldrich.

N,N-tetramethylethylenediamine (TEMED, used as activator for the polymerization) was obtained from Acros Organics.

2.2. Methacrylation and cross-linking of the polysaccharides

The reaction conditions are outlined in Table 1. The polysaccharide solution was prepared by stirring overnight. Subsequently, the MAAH was added dropwise. The reaction was left to proceed for the designated time, after which a dialysis was performed for 72 hours whilst changing the dialysis water twice per day. The resulting solution of methacrylated polysaccharide (AlgMOD or ChiMOD) was frozen and the water removed via lyophilization using a Christ freeze-dryer alpha 2-4-LSC at -85 °C and 0.37 mbar.

Table 1: Methacrylation reaction conditions.

Polysaccharide	Solvent	Polymer concentration [w%]	MAAH added[eq]	pH	Temperature	Stirring time
Alginate	Milli Q	2.00	2.00	8	r.t.	24 h
Chitosan	2 v% AcOH	1.50	0.80	5	r.t.	3 h

The cross-linking reaction of the methacrylated polysaccharides with either DMAEMA or DMAPMA took place by preparing a certain amount of modified polysaccharide, monomer and TEMED in a solvent (all amounts and solution types are specified in Table 2). The mixture was placed under nitrogen atmosphere by flushing the system after which the temperature was raised if needed. Subsequently APS was added to initiate the reaction. After 24 hours, the SAP was submersed in an excess of demineralized water for 24 hours to remove unreacted products after which it was frozen and dried by lyophilization. Finally the resulting material was grinded into a powder with an A11 basic Analytical Mill.

Table 2: DMAEMA/DMAPMA cross-linking reaction conditions.

Poly-saccharide	Solvent	Temperature [°C]	Polysaccharide concentration [w%]	Monomer conc. [w%]	TEMED conc. [v%]	APS conc. [w%]
AlgMOD	Milli Q	45	2	14	0.48	0.32
ChiMOD	6 v% AcOH	r.t.	2	14	0.96	0.64

2.3. Characterization of the synthesized SAPs

Gel fraction quantification

The gel fraction was determined by weighing a dried sample of the hydrogel directly after the cross-linking reaction before and after washing for 24 hours.

Moisture uptake measurements using dynamic vapor sorption (DVS)

Moisture uptake at 0, 30, 60, 90 and 95% RH was determined with a Cahn microbalance. Each subsequent step was initiated when a change in sample mass lower than 0.002 mg/min

was observed. The cycle continued with a desorption phase where the same sequence of RH levels was used but in reverse order.

Determination of the swelling capacity
0.2 g SAP (m_{SAP}) was added to 100 ml swelling medium (m_0) (i.e. demineralized water or cement slurry filtrate) and the pH was adjusted with NaOH or HCl if necessary. After 3 hours of incubation, the liquid was brought over a filter to remove the swollen hydrogel. The filtrate (m_f) was weighed and the swelling capacity in g absorbed water per g SAP was calculated using Equation 1:

$$S = (m_0 - m_f)/m_{SAP} \quad (1)$$

Cement slurry filtrate was prepared by stirring ordinary Portland cement in demineralized water for three hours. The suspension was subsequently filtered to remove solid cement particles. The resulting liquid is cement slurry filtrate with a pH of approximately 12.6.

2.4. Influence of SAP incorporation on mortar strength
A standard mortar mixer was used to prepare mortar samples according to the EN 196-1 standard by mixing 450 g (22 w%) ordinary Portland cement (CEM I 52.5 N; 510 kg/m^3) with 225 g (11 w%) water and 1350 g (67 w%) silica sand 0/2 (1530 kg/m^3). On top of these amounts, 2.25 or 4.50 g SAP (ChiMOD DMAPMA) for 0.5 and 1 w% respectively and additional water to account for the water uptake of the hydrogel (based on the water uptake in cement filtrate) were added. After a curing period of 28 days, the mortar samples were tested for their flexural and compressive strength by means of a three-point-bending test followed by a compression test on the resulting halves (complying to the EN 196-1 standard) using the Walter + Bai DB 250/15 machine.

2.5. Self-healing efficiency
The composition of the mixtures used for measuring the self-healing efficiency can be found in Table 3. First, the cement (CEM I 52.5N), fly ash (Class F) and SAPs (except for the reference mixture) were equally distributed with a mortar mixer. Then, water and superplasticizer were added and mixed for 30s at 140 rotations per minute (rpm). The fine silica sand (M34, Sibelco) was added during the next 30s at 140 rpm. To ensure a homogenous dispersion of all components, the speed was increased for the following 30s to 285 rpm. The edges of the bowl were then scraped during 30s and the mixture was resting for a period of 60s. Subsequently, at a speed of 140 rpm, synthetic PVA microfibers (RECS 15x8, Kuraray) were slowly added during 30s. The final step was mixing for 60s at 285 rpm. Molds (160 x 40 x 10 mm³ samples) were filled with the mixture. The samples were demolded after 48h and were stored at a relative humidity of 95 ± 5% and a temperature of 20 ± 2°C until the age of 28 days. Series used within this study consisted of a minimum of 3 samples with 2 v% of PVA microfibers to induce multiple cracking.

Cracks were created in the specimens by a four-point bending test at the age of 28 days. A servo hydraulic testing system (Walter+Bai DB 250/15) ensured a displacement-controlled test (0.0015 mm/s to imitate a quasi-static load). The lower span was 140 mm and the upper loading span was 40 mm. The strain at the bottom side of the specimen was limited to 1%,

theoretically calculated from the curvature and the vertical displacement during loading. This strain is lower than the maximum possible strain upon failure of such a strain-hardening specimen, so the service cracks could be studied before opening due to pullout of the fibers. After cracking, the samples were stored in a room at 20 ± 2°C by applying wet-dry cycles (alternatingly stored in water for 12h and at a relative humidity of 60% for 12h).

After a period of 28 days of healing, the specimens were reloaded in four-point bending until failure and the regain in first-cracking strength, obtained during the first and second loading cycle, was compared [13].

Table 3: Mortar composition of the studied mixtures.

Sample Code	m% SAP	Cement [kg/m³]	Fly ash [kg/m³]	Sand [kg/m³]	Water [kg/m³]	Additional water [kg/m³]	Super-plast [kg/m³]	Fibers [kg/m³]
Reference	0	608	608	426	365		12	26
ChiMOD DMAPMA	0.5	584	584	409	350	39	12	26
	1	577	577	404	346	51	12	26

3. Results and discussion

3.1 Characterization performed on SAP

Gel fraction quantification

Gel fraction of a SAP is the percentage of dry weight that is incorporated in the polymer network. It is calculated by weighing the dried material before and after purification, where the unreacted agents and non-covalently linked oligomers are removed. It gives an indication on the efficiency of the cross-linking reaction. All measurements were performed in triplicate and the results are shown in Table 4. It could be seen that the polymers with DMAEMA showed a higher gel fraction compared to their DMAPMA counterpart. This could be explained partly because the structure of the SAPs containing DMAPMA is more brittle and as such more prone to becoming damaged during purification.

Table 4: Gel fraction results.

Material	Gel fraction	Standard deviation
AlgMOD DMAEMA (high DS)	80.1	0.35
AlgMOD DMAPMA (high DS)	64.7	1.39
ChiMOD DMAEMA	64.7	5.01
ChiMOD DMAPMA	49.0	10.67

Moisture uptake capacity of the SAPs using DVS

To identify the behavior of the hydrogels in mortar or concrete in conditions where no direct contact with water is possible, moisture uptake capacity measurements were performed. In some applications, water cannot infiltrate into the formed cracks and only humidity from the

air can be absorbed. If this uptake capacity is high enough, these cracks could be partially sealed already.

The results are shown in Figure 1. It could be observed that the hydrogels, especially the ones containing DMAPMA have a high moisture uptake capacity (even up to 120% its own weight for ChiMOD DMAPMA). All materials showed a negligible hysteresis, which implies that all moisture initially absorbed will again desorb at equal relative humidity (RH) levels. This is advantageous as a slow desorption of this water during the curing of mortar leads to a gradual drying. This also lowers the probability of cracks to manifest during curing. In addition, this released water can lead to the deposition of $CaCO_3$ from dissolved $Ca(OH)_2$ and CO_2, which increases the self-healing of mortar.

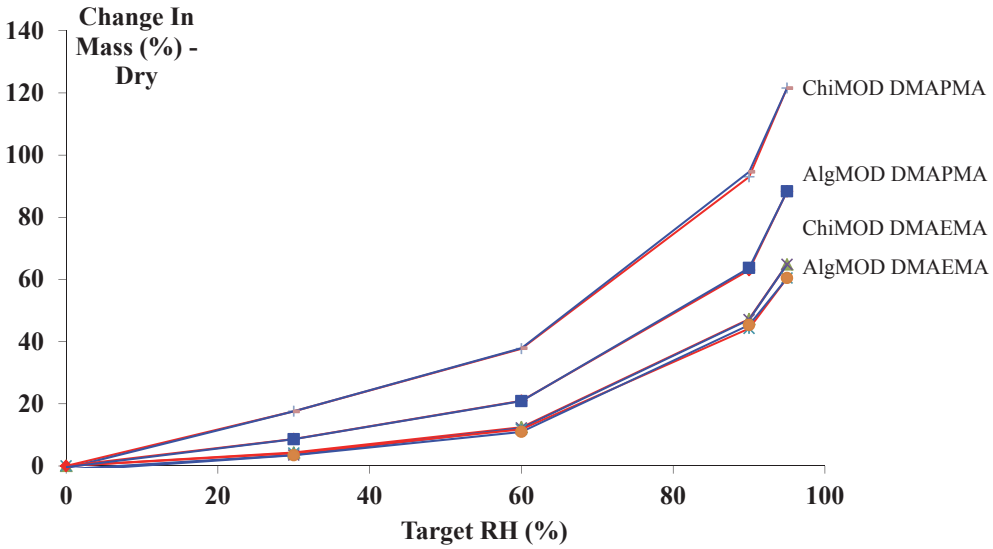

Figure 1: Sorption and desorption isotherms of the SAPs measured by DVS.

Swelling capacity as a function of the composition of SAP

The results of the swelling capacity are shown in Figure 2 (a,b). To understand these results, a first explanation needs to be given on the pH-responsiveness of these polymers.

Alginate contains carboxylic acid groups which will become negatively charged at pH higher than its pKa (~3.5). The amine group in the basic monomers becomes positively charged at pH values lower than the pKa values (8.4 for DMAEMA and 8.9 for DMAPMA). Chitosan also contains amine groups and has a pKa ~6.5. Similar charges will repel each other and create more possibility for swelling. The swelling tests have been performed in aqueous solutions with a varying pH (pH 3, 8 and 12) to indicate the pH-responsiveness of the SAPs.
Due to the combination of the carboxylic acids from alginate and the amine groups of the monomers, the SAPs (AlgMOD DMAEMA and AlgMOD DMAPMA) did swell at pH 3 (only positively charged amine groups) and at pH 12 (only negatively charged carboxylic acid

groups) as seen in Figure 2b. However, an association of the positive and negative charges at pH 8 leads to a denser physically cross-linked network, with less free volume for the absorption of water. This is the opposite trend as anticipated. For that reason these SAPs will be less useful in the intended application.

Chitosan in combination with the monomers is much more promising. In this case, at a pH of 12, no amines are positively charged and a low swelling is measured. However at a pH of 8, the amines of DMAEMA or DMAPMA start to become positively charged, leading to an increased swelling. At pH 3, both the amines of the monomers and of chitosan become positively charged and lead to an even further increase of the swelling. It is evident that these are better materials to incorporate in mortar. As the swelling is similar for both materials, but the moisture uptake capacity of ChiMOD DMAPMA is much higher than ChiMOD DMAEMA, the first one will be further tested on its effect on the strength and self-sealing and -healing efficiency.

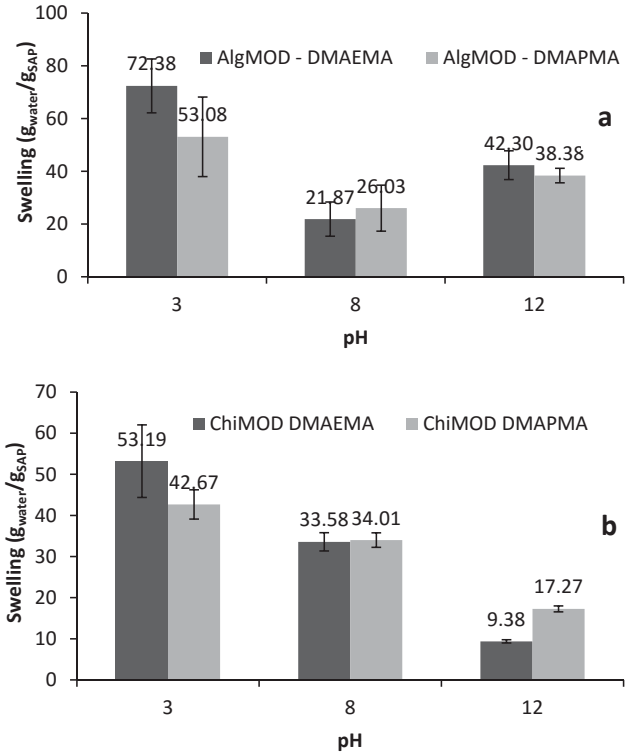

Figure 2: Swelling capacity of the SAPs. AlgMOD DMAEMA & AlgMOD DMAPMA (a), and ChiMOD DMAEMA & ChiMOD DMAPMA (b).

3.2. Influence of mortar strength upon SAP incorporation

Chosen as the best material of the above-mentioned series, ChiMOD DMAPMA has been incorporated in mortar in 2 different amounts (0.5 m% and 1 m% in function of the amount of cement) to indicate the effect on the strength. After a curing period of 28 days, the samples were tested by means of three point bending and compression strength tests (Table 5).

Table 5: Influence of SAP incorporation on mortar strength

	Bending strength			**Compression strength**		
Material	Mean	Stdev	% Loss	Mean	Stdev	% Loss
Reference	8.6	0.2		68.4	1.1	
ChiMOD DMAPMA 0.5 m%	8.1	0.14	5.8	58.1	1.4	15.1
ChiMOD DMAPMA 1.0 m%	7.3	0.4	15.1	51.8	1.3	24.3

Additional water was added to compensate for the absorption of mixing water by the polymers and to create mixtures showing a similar workability as the reference material with a water-to-cement ratio of 0.50 [8]. Samples containing SAPs have an effect on the strength, however this is very limited compared to addition of specific synthetic SAPs [8]. The higher the addition of SAP, the more pronounced the effect is on the strength, when using a high water-to-cement ratio [10]. Upon addition of ChiMOD DMAPMA, the bending strength decrease remains below 15% and for the compression strength below 24% (addition up to 1 m% SAP in function of the added amount of cement).

3.3. Self-healing efficiency of mortar samples by incorporation of SAPs

A different mixture was used for the self-healing efficiency as microfibers were needed to create several small cracks instead of 1 large crack. If fibers were added to the original mixture, the slump flow would not be as anticipated. Therefore this mixture was adjusted to the one as described in [13]. Due to the use of microfibers, multiple cracking was obtained. Multiple smaller cracks will make sure that enough SAPs are available for self-healing and will lead to a better autogenous healing as smaller crack widths show better healing compared to larger crack widths. In the samples with an addition of SAPs, macropores were formed during the mixing and hardening of the mortar, which could act as crack initiators [13]. This will increase the ductile behavior of the mortars. To study the self-healing capacity of the mortars with or without SAPs, the samples were cracked up to 1% strain. This was done to study the crack widths occurring during the lifetime of a structure, but not to complete failure. As the samples were stored in wet-dry cycles, a large amount of water was available for autogenous healing. To give an indication on the self-healing efficiency of the mortars, the strength regain after 28 days of self-healing was compared between the samples with and without SAP addition. However, a few things should be taken into account when comparing these results.

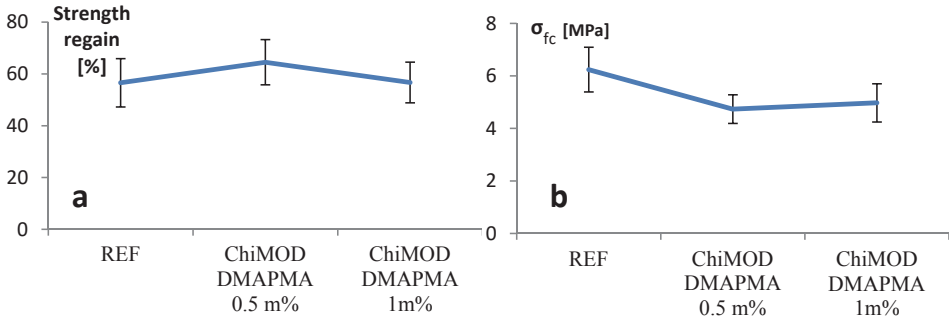

Figure 3: (a) strength regain values of the mortar samples and (b) first cracking strength.

As can be seen in Figure 3a, there is no significant difference ($p < 0.05$) between the reference and mortar with ChiMOD DMAPMA (1 m% addition). When comparing the first cracking strength ($\sigma_{fc,}$ Figure 3b), there is also no significant difference. However, there is a difference in the crack size distribution. Microscopy has shown that 90% of the cracks were between 1 and 47 µm for the reference and between 2 and 63 µm for ChiMOD DMAPMA 1 m%, meaning the latter would need an improved self-healing efficiency, to obtain a similar strength regain as the reference. This means that addition of 1 m% would lead to a reduced autogenous healing compared to the reference material. On the other hand, the water available in the SAPs should be used for improved autogenous healing. In literature, cracks up to 130 µm are able to close when using commercial SAPs. Here, partial recovery can be seen.

When now comparing the reference with ChiMOD DMAPMA 0.5 m%, a small increase in the strength regain was observed (however not a significant difference). σ_{fc} was actually significantly lower than the reference material and when investigating the crack size distribution, 90% of the cracks were situated between 1 and 33 µm. The combination of smaller cracks and lower σ_{fc}, could explain the small increase (again, not significant) in the strength regain.

It could be concluded that especially an addition of 1 m% SAP induced the strongest self-healing as larger cracks needed to be sealed and in addition a similar strength regain was obtained compared to the reference mortar. However, the improvement was more limited than envisaged, mainly due to the high self-healing capacity of the reference mortar, which was a fiber reinforced cementitious composite.

Further research will focus on the functionalization of these new types of SAPs, to further improve self-healing properties without reducing the strength.

4. Conclusion

It can be concluded that bio-based pH-responsive superabsorbent polymers could be very promising for self-healing of cracks in mortar and concrete. These SAPs showed a strong moisture uptake capacity up to 120% of the original weight and a swelling capacity up to 50-

70 times their weight, especially at a lower pH. The polymers will thus not swell during the mixing process (alkaline condition), but will swell when cracking occurs and water enters the crack (neutral to acidic condition). Therefore, upon incorporation of ChiMOD DMAPMA in mortar, the samples showed only a limited strength reduction (< 24% when adding 1 m% SAP, in function of the added amount of cement). An addition of 1m% also lead to a stronger self-healing capacity compared to reference samples, although the difference was limited due to the high self-healing capacity of the reference. These results can conclude that ChiMOD DMAPMA could be a promising polymer for self-healing of cracks. Further research could be performed to further optimize these materials for an even stronger self-healing.

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