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Combinatory approach of methacrylated alginate and acid monomers for concrete applications

Arn Mignon [a,b], Dries Devisscher [b,c], Geert-Jan Graulus[b], Birgit Stubbe[b], José Martins[d], Peter Dubruel [b], Nele De Belie [a,*] and Sandra Van Vlierberghe [b,*]

[a] Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, Technologiepark Zwijnaarde 904, B-9052 Ghent, Belgium.
Arn.Mignon@ugent.be, Nele.DeBelie@ugent.be

[b] Polymer Chemistry & Biomaterials Research Group, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281, Building S4-bis, B-9000 Ghent, Belgium.
Arn.Mignon@ugent.be,Peter.Dubruel@ugent.be,Sandra.VanVlierberghe@ugent.be,
Geertjan.Graulus@ugent.be, Birgit.Stubbe@ugent.be

[c] Design & Synthesis of Organic Semiconductors, Institute for Materials Research, Hasselt University, Agoralaan 1 – Building D, 3590 Diepenbeek, Belgium
Dries.Devisscher@uhasselt.be

[d] NMR and Structure Analysis Unit, Department of Organic Chemistry, Ghent University, Krijgslaan 281, Building S4 bis, B-9000 Ghent, Belgium
Jose.Martins@UGent.be

*Corresponding author: Sandra Van Vlierberghe
Krijgslaan 281, S4-bis
B-9000 Ghent, Belgium
e-mail: Sandra.VanVlierberghe@UGent.be
tel: 003292644508
fax: 003292644998

Abstract:
Polysaccharides, and especially alginate, can be useful for self-healing of cracks in concrete. Instead of weak electrostatic bonds present within calcium alginate, covalent bonds, by methacrylation of the polysaccharides, will result in mechanically stronger superabsorbent polymers (SAPs). These methacrylated alginate chains as backbone are combined with two acrylic monomers in a varying molar fraction. These SAPs show a moisture uptake capacity up to 110% their own weight at a relative humidity of 95%, with a negligible hysteresis. The swelling capacity increased (up to 246 times its own weight) with a decreasing acrylic acid/2 acrylamido-2-methylpropane sulfonic acid ratio. The SAPs also showed a thermal stability up to 200°C. Interestingly, the SAP composed of alginate and acrylic acid exerted a very limited decrease in compressive strength (up to 7% with addition of 1 wt% SAP) rendering this material interesting for the envisaged self-healing application.

Keywords:
polysaccharide; alginate; self-healing; concrete; swelling potential; compressive strength

1. Introduction

Reports have been presented in literature covering synthetic superabsorbent polymers (SAPs) used in concrete for various applications such as internal curing (Mechtcherine et al., 2014; Viktor Mechtcherine, 2006), frost resistance (Jensen, 2013; Laustsen, Hasholt & Jensen, 2013) and self-sealing and -healing of cracks (Mignon et al., 2014; Snoeck, Van Tittelboom, De Belie, Steuperaert & Dubruel, 2012; Snoeck, Van Tittelboom, Steuperaert, Dubruel & De Belie, 2014). The use of synthetic SAPs has been proven to be promising as a smart internal solution for this latter application (Mignon et al., 2014; Mignon et al., 2015b; Snoeck, Van Tittelboom, Steuperaert, Dubruel & De Belie, 2014). However, these synthetic materials often compromise the material strength, which is undesired in the construction industry. On the one hand, the SAP particles will cause internal curing by releasing their entrained mixing water, stimulating the densification and further hydration of the cementitious matrix and reducing autogenous shrinkage and hence, the risk at early age cracking. These consequences can lead to an increase of the overall material strength. Conversely, after the release of the entrained water by the SAPs, air-filled macropores will remain present in the matrix, which generally leads to a decrease of the overall concrete strength (Hasholt, Jensen, Kovler & Zhutovsky, 2012; Laustsen, Hasholt & Jensen, 2013; Snoeck, Schaubroeck, Dubruel & De Belie, 2014). As for self-sealing (Snoeck, Steuperaert, Van Tittelboom, Dubruel & De Belie, 2012) and self-healing applications (Snoeck, Schaubroeck, Dubruel & De Belie, 2014; Snoeck, Van Tittelboom, Steuperaert, Dubruel & De Belie, 2014) high SAP amounts are required (up to 1 % relative to cement mass), this macropore formation becomes more critical especially when high amounts of additional water are used to compensate for the loss in workability. Previous research has proven that polysaccharides and especially alginate, are very promising as starting materials for self-sealing and -healing of cracks. However, instead of the weak electrostatic bonds present within calcium alginate which are prone to disintegration in the presence of monovalent cations (Bajpai & Sharma, 2004), covalent linkages generally result in mechanically superior SAPs (Povh & Rosina, 2005). One way to create covalent bonds in a SAP network based on polysaccharides is by first modifying them with methacrylic anhydride (MAAH) (Chou, Akintoye & Nicoll, 2009; Chou & Nicoll, 2009). MAAH can be used to enable cross-linking of the polysaccharides. In the case of alginate, the hydroxyl groups will react with the anhydride resulting in methacrylated alginate. These methacrylate functions can be used to execute a free radical polymerization in the presence of acrylic monomers.

Acrylic acid (AA) has already been proven to be a widespread used monomer for the development of synthetic SAPs, often in combination with other acrylic monomers such as acrylamide (Ding, Xiao, An & Jia, 2006; Mohammad J. Zohuriaan-Mehr 2008; Nesrinne & Djamel, 2013; Zhang, Cui, Yin, Li, Liao & Cai, 2011; Zhou et al., 2003). Another interesting monomer is 2-acrylamido-2-methylpropanesulfonic acid (AMPS) as this hydrophilic, sulfonic acid possesses a large swelling capacity and has already been used in a variety of applications going from water treatment (Kang & Cao, 2012; Yu et al., 2011) and drug delivery (Pourjavadi, Barzegar & Zeidabadi, 2007) towards other biomedical applications (Anirudhan & Sandeep, 2011; Keogh, 1995; Keogh, Hobot, Eaton, Jevne & Bergan, 1995) and personal care (Abdel-Azim, Farahat, Atta & Abdel-Fattah, 1998; Cahalan & Coury, 1986; Lundmark, Melby & Chun, 1978).

The present manuscript reports on the development and characterization of SAPs based on methacrylated alginate as backbone combined with a varying molar fraction of a carboxylic acid (AA) and/or a sulfonic acid (AMPS). The degree of methacrylation after modification will be determined by proton nuclear magnetic resonance spectroscopy. After polymerization, the gel fraction and particle size distribution will be identified. The chemical structure of the synthesized SAPs will be verified through attenuated total reflectance-infrared (ATR-IR) spectroscopy. High resolution magic-angle spinning (HR-MAS) ^{1}H-NMR spectroscopy will be used to identify the polymerization efficiency. In addition, the sorption and desorption of moisture at different relative humidities will be measured by dynamic vapor sorption (DVS) measurements. It is also important to identify the swelling degree in aqueous (ultrapure water and demineralized water) and cement filtrate solutions. Additionally, the thermal stability is evaluated using thermogravimetric analysis (TGA). Finally, the influence of these SAPs on the strength of mortar is also determined.

2. Materials and methods

2.1. Materials

2-Acrylamido-2-methylpropane sulfonic acid (AMPS), ammonium persulfate (APS), sodium alginate (NaAlg, M/G ratio of 2.3, Mw of 76 kDa and a Đ of 4.6) and methacrylic anhydride (MAAH) have been bought from Sigma-Aldrich (Bornem, Belgium). Acrylic acid (AA) and N,N,N',N'- tetramethylethylene-diamine (TEMED) originated from Acros Organics (Geel, Belgium). N,N'-methylene bisacrylamide (MBA) came from Merck (Nottingham, UK). The paper filters (retention of 8 – 12 µm) were purchased at Munktell filters (Bärenstein, Germany).

2.2. Modification of alginate backbone with methacrylate moieties

A derivatization of alginate with methacrylic anhydride (MAAH), based on a reaction of the hydroxyl moieties of the polysaccharide backbone with the anhydride, was carried out to incorporate methacrylate groups for network formation. A 2 wt% sodium alginate solution was prepared in demineralized water using a mechanical stirrer. Subsequently, MAAH was added dropwise to the solution. The added amount corresponded with 2 equivalents of MAAH with respect to the hydroxyl groups from alginate. During the reaction, methacrylic acid was released which lowers the pH of the reaction. However, the acidity of the mixture was constantly monitored and the pH was increased to 8 by adding small amounts of a 5 M sodium hydroxide (NaOH) solution. Conversely, the pH should not be too high to avoid hydrolysis of the ester in the reaction product. The mixture was reacted at room temperature for 24 hours after the addition of MAAH. Afterwards, dialysis (12 – 14 kDa) was performed for 72 hours while changing the dialysis water twice a day to remove unreacted agents and formed methacrylic acid. The resulting solution afforded modified alginate (algMOD) by lyophilization.

2.3. Detailed characterization of the synthesized SAPs

After polymerization, unreacted particles were removed from the end product via dialysis. By measuring the dry weight of the sample before and after purification during 24 hours, the gel fraction could be determined using the following equation:

$$G\ [\%] = {}^{W}/_{W_0} \quad (1)$$

W = mass of the dry insoluble part of the sample

W_0 = initial dry mass of the sample

To examine the resulting particle size diameters of all grinded materials (grinded with an A11 basic Analytical Mill), a Zeiss Axiotech optical microscope was used together with the digital image capturing software ZEN core and the analysing software ImageJ. A sample population > 100 has been used. The statistical analysis was performed by creating a size distribution curve.

The SAP powder was subsequently characterized using attenuated total reflectance infrared (ATR-IR) spectroscopy. A BioRad FTS 575C combined with a MKII Golden Gate setup equipped with a diamond crystal from Specac was used for all experiments. These results were analysed with the Bio-Rad Win-IR Pro software.

The ^{1}H-NMR spectra were obtained by dissolving the samples in D_2O (10 mg/ml) and recording the samples at room temperature on a Varian Inova 400 MHz spectrometer using a 5 mm four-nucleus PFG probe with water suppression.

High Resolution Magic-Angle Spinning NMR (HR-MAS ^{1}H-NMR) spectroscopy analysis of the developed SAPs was performed on a Bruker Avance II 700 spectrometer (700.13 MHz) using a HR-MAS probe equipped with a ^{1}H, ^{13}C, ^{119}Sn and gradient channel. The spinning rate was set to 6 kHz. Samples were prepared by placing a small amount of freeze-dried material inside a 4 mm zirconium oxide MAS rotor (80 µL). 30 µL D_2O was added to the rotor, allowing the samples to swell. The samples were homogenized by manual stirring prior to analysis. A teflon® coated cap was used to close the rotor.

Dynamic vapor sorption (DVS) experiments were applied as described earlier in (Mignon et al., 2015a) with systematic steps of 20, 40, 60, 80, 90 and 95% RH.

<u>Swelling tests performed in ultrapure and demineralized water</u>

The swelling capacity of the SAPs was determined as the mass change between the freeze-dried and the swollen (cfr. saturated) state. A mass of 0.15 - 0.20 g polymer was incubated in 100 mL of aqueous solution. After 3h incubation, a funnel and a filter were used to capture the water that was not absorbed by the SAPs. By calculating the difference between the initially added and the filtered water, the residual water inside the material could be determined together with the swelling capacity of the material using Equation (5):

$$Swelling\ capacity = {}^{(m_0 - m_{filter})}/_{m_{SAP}} \quad (5)$$

where m_0 is the initially added water mass [g], m_{filter} represents the mass of the water going through the filter [g] and m_{SAP} is the added mass of dried SAP (i.e. 0.20 g). The filtration paper was typically saturated prior to the filtration to exclude its influence on the mass of the filtered water.

<u>Swelling tests in cement filtrate solutions</u>

Cement filtrate (CF) was made by mixing 10 g ordinary Portland cement (OPC) and 100 mL demineralized water for three hours with a mechanical stirrer, followed by filtration to remove the cement particles and collecting the solution. The same conditions as for aqueous solutions were used for further analysis. All swelling tests were performed in triplicate.

The thermal properties were analyzed using thermogravimetric analysis (TGA) using a TA-instruments Q-50 Thermogravimetric Analyzer as described earlier in (Mignon et al., 2015b) with a maximal temperature of 600°C and a starting equilibrium temperature of 30°C.

2.4. Bending and compression strength measurements

Mortar samples were manufactured by a standard mortar mixing procedure, as described in detail in EN 196-1 to investigate the influence of the addition of SAPs on the flexural and compression strength of mortar samples. Flexural and compressive strength were measured at the age of 28 days by means of a three-point-bending test followed by a compression test on the resulting halves following the Standard NBN EN 196-1 and described in detail in (Mignon et al., 2015b).

3. Results and discussion

3.1. Methacrylation of alginate through modification with methacrylic anhydride

In a first step, alginate was methacrylated yielding algMOD. The degree of methacrylation (DM, or the degree of substitution, DS) (i.e. the amount of double bonds incorporated on alginate) has a strong influence on the physical properties as well as the swelling capacity of the formed SAP. For that reason, it is important to calculate the DS using ^{1}H NMR spectroscopy (as described in section 2.6).

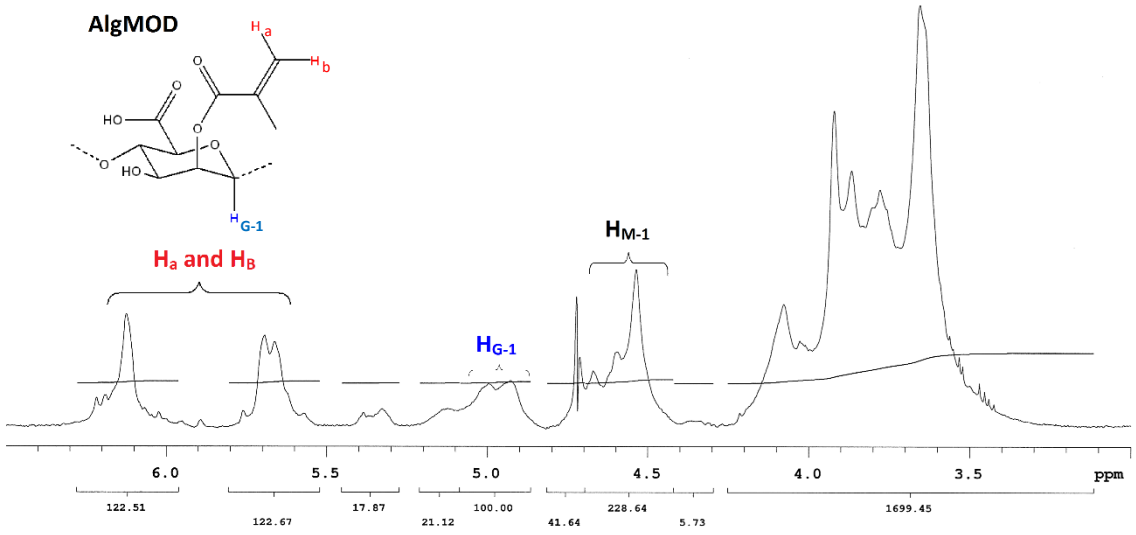

Figure 1: ^{1}H NMR spectrum of algMOD with annotation of the relevant peaks for the calculation of the DS (H_a and H_b as protons connected to the C=C bond, a proton on the α-l-guluronic acid structure (H_{G-1}), and a reference proton on the β-d-mannuronic acid (H_{M-1}, not shown on molecular structure).

The obtained spectra were analyzed by comparing the characteristic peaks of the methacrylate moieties corresponding to the vinyl protons at 5.73 and 6.16 ppm with the reference peak from the alginate backbone at 4.97 ppm. As the latter corresponds with the anomeric carbon of the guluronic acid block (G-units), the G-value had to be calculated and incorporated as a correction factor due to the presence of mannuronic acid (M-units). Therefore, the relative proportion of the G-units compared to the total amount of G- and M-units had to be determined by using Equation 2. Subsequently, the average of the peaks of the methacrylate groups was calculated and used to compute the degree of substitution (DS) per repeating unit by applying Equation 3. To obtain the DS with respect to the hydroxyl groups, this value had to be divided by two as the considered repeating unit (G-unit) possessed two hydroxyl groups.

$$G\ [\%] = \frac{H_{G-1}}{H_{M-1}+H_{G-1}} = \frac{I_{4.97ppm}}{I_{4.58ppm}+I_{4.97ppm}} * 100\% \quad (2)$$

$$DS\ [\%] = G * \frac{\frac{H_a+H_b}{2}}{H_{G-1}} = G * \frac{\frac{I_{5.73ppm}+I_{6.16ppm}}{2}}{I_{4.97ppm}} \quad (3)$$

The protons H_{G-1}, H_{M-1}, H_a and H_b are related to the intensity of their related peaks on the NMR spectrum, seen further in Figure 1. Using Equations 2 and 3, a relative concentration of guluronic acid units or G-content of 30.5% and a DS of 18.7% as a function of the present hydroxyl groups were determined. The latter implies that almost one out of five functional hydroxyl groups or one of every three repeating units (37.4%) have been modified.

3.2. SAP development and characterization

After modification, methacrylated alginate (algMOD) was combined with the monomers (AA and AMPS) to create a cross-linked network through free radical polymerization. AMPS was selected as second monomer to compare the effect of a carboxylic acid versus the incorporation of a sulfonic acid with respect to the swelling capacity as well as the influence on the mortar strength. AlgMOD combined with AA forms a strong and transparent solid gel while a decrease in AA/AMPS ratio leads to a more brittle gel. The composition and nomenclature of the SAPs is given in Table 1.

Table 1: Overview of theoretical chemical composition of the developed SAPs and the gel fraction. The algMOD fraction was added in addition to the total monomer amount.

Sample	$\frac{\boldsymbol{AlgMOD}}{\boldsymbol{AA}+\boldsymbol{AMPS}}$ g/g	AA mol%	AMPS mol%	Gel fraction (%)
p(alg(1)_AA_{100}/$AMPS_0$(7))	1/7	100	0	85.3 ± 1.2
p(alg(1)_AA_{75}/$AMPS_{25}$(7))	1/7	75	25	80.9 ± 2.6
p(alg(1)_AA_{50}/$AMPS_{50}$(7))	1/7	50	50	61.3 ± 2.2
p(alg(1)_AA_{25}/$AMPS_{75}$(7))	1/7	25	75	58.9 ± 1.3
p(alg(1)_AA_0/$AMPS_{100}$(7))	1/7	0	100	42.7 ± 6.2

Table 1 also shows that a lower AA/AMPS ratio leads to a significant decrease in the gel fraction. On the one hand, the materials containing more AMPS were more brittle and thus more prone to become damaged during purification. In addition, the higher polarity of AMPS could have resulted in an increased repulsion between negatively charged carboxylate groups on the alginate backbone and sulfate moieties on the AMPS monomer, thereby hindering the crosslinking reaction.

Smaller particles have a higher surface area which can have an influence on a.o. the moisture uptake capacity. In addition, upon incorporation in mortar, these smaller particles will lead to more smaller pores compared to larger SAPs. All materials showed a similar particle size for d_{10} and d_{50} (see Table 2). In the table, d_x indicates the diameter where x percentage of the particles is smaller or equal to. Approximately half of the particles were characterized by a diameter of 20 µm or lower. However, the d_{90} values show that there was a small variation between the SAPs, which can be related to the duration of the grinding. However, the difference was quite limited and all diameters ranged between 50 – 80 µm.

Table 2: Particle size ranges of the algMOD - AA/AMPS SAPs where d_{10}, d_{50} and d_{90} indicate the percentage of particles (10%, 50% and 90%) with a diameter smaller or equal to x µm .

Material	d_{10} [µm]	d_{50} [µm]	d_{90} [µm]
p(alg(1)_AA_{100}/$AMPS_0$(7))	9-10	20-21	80
p(alg(1)_AA_{75}/$AMPS_{25}$(7))	8-9	20-21	47-48
p(alg(1)_AA_{50}/$AMPS_{50}$(7))	8-9	18-19	48-49
p(alg(1)_AA_{25}/$AMPS_{75}$(7))	10-11	21-22	75-76
p(alg(1)_AA_0/$AMPS_{100}$(7))	10-11	20-21	67-68

3.3. Chemical structure confirmation and cross-linking efficiency assessment

ATR-IR spectroscopy has been performed on the p(alg_AA/AMPS) SAPs (see Figure 2). The S=O stretch at 1040 cm^{-1} of the sulfonic acid ((a) in Figure 2), the N-H stretch of the secondary amides between 3500 and 3100 cm^{-1} and at 1550 cm^{-1}(b) and the C=O stretch of the amides at 1650 cm^{-1} (c) are clearly stronger present with an increasing amount of AMPS.
The C=O stretch of the acid moiety at 1700 cm^{-1} (d) is on the other hand strong for p(alg(1)_AA_{100}/$AMPS_0$(7)) due to the high amount of AA. These peaks are found by comparing to earlier performed research (Athawale & Lele, 1998; Athawale & Lele, 2000; Najjar, Yunus, Ahmad & Rahman, 2000; Rosa, Bordado & Casquilho, 2003).
These results give a qualitative indication of the presence of the polysaccharide and the monomers as well as an increase or decrease of the intensity of certain peaks which is related to the variation of the AA/AMPS ratio.

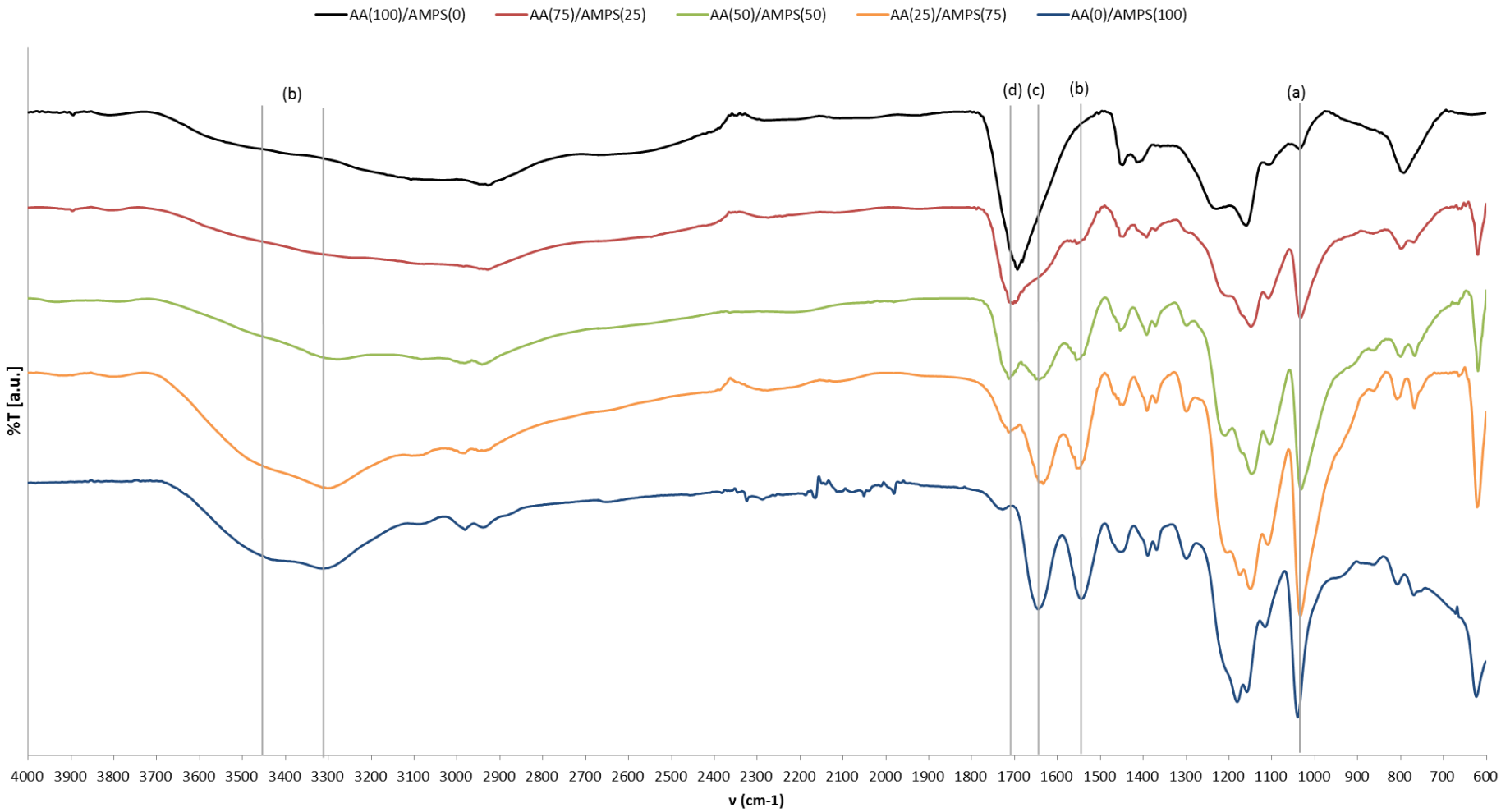

Figure 2: FTIR spectra of the algMOD - AA/AMPS SAPs with annotation of the most relevant peaks. The samples are abbreviated by the molar ratio of the incorporated monomers according to: AA(x) /AMPS(y).

HR-MAS ^{1}H-NMR spectroscopy was used as a technique to confirm the polymerization (cross-linking) efficiency. The peaks corresponding to protons from the C=C double bonds from either the methacrylate functionalities introduced in algMOD or from the monomers are apparent in the range of 5.5 – 6.5 ppm (as indicated in Figure 1 for algMOD). After polymerization, these signals have completely disappeared, as shown in Figure 3 (i.e. p(alg(1)_AA_{50}/$AMPS_{50}$(7)) as an example). These peaks have shifted to the right (1.5 – 2.5 ppm) by conversion of the double bond protons into alkane protons, adjacent to an electronegative group.

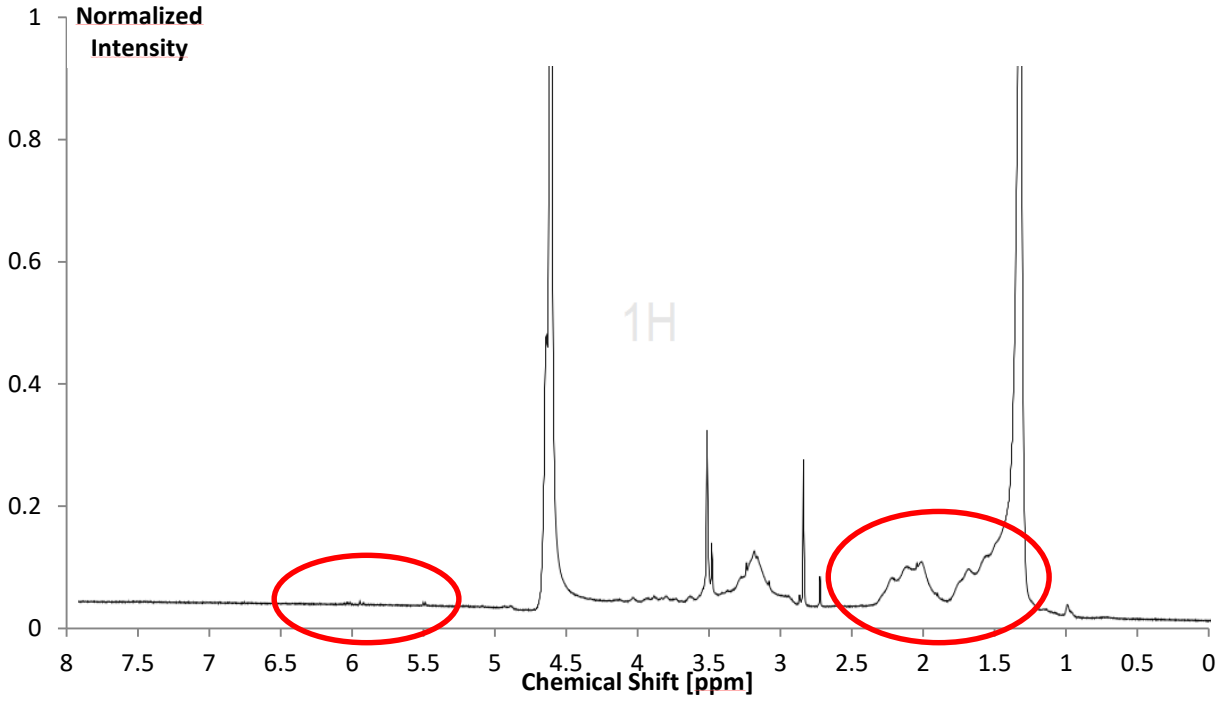

Figure 3: HR-MAS ^{1}H NMR spectrum of p(alg(1)_AA_{50}/$AMPS_{50}$(7)). The absence of peaks corresponding to double bond protons (situated between 5.5 and 6.5 ppm) from either algMOD, AA or AMPS confirms the success of the cross-linking reaction.

3.4. Determination of the moisture uptake capacity of the SAPs via dynamic vapor sorption

The moisture uptake capacity of the SAPs has been assessed to identify their behavior in mortar or concrete, when no direct ingress of water or rain is possible upon crack formation. If these SAPs can significantly absorb moisture in humid environments, the cracks may be partially sealed. The results (see Figure 4 (a)) show that with a decrease of the AA/AMPS ratio, the moisture uptake capacity increases, especially at high relative humidity (RH). The values range between 53.6 and 109.8% at a RH of 95%. Materials with ≥ 50 mol% AMPS can even take up more than their original weight in moisture at a RH of 95%. In addition, these materials show a negligible degree of hysteresis. As a result, all moisture taken up can also be completely desorbed again. Indeed, concrete constructions that are not exposed to humid environments can thus still retain a certain amount of moisture from air at the crack faces. In a subsequent stage, the SAPs are likely to completely deliver this moisture to remaining unreacted cement particles, which can lead to formation of new cement hydration products and deposition of $CaCO_3$ from dissolved $Ca(OH)_2$ and CO_2, thereby contributing to the development of self-healing applications (Snoeck, Van Tittelboom, Steuperaert, Dubruel & De Belie, 2014).

The reason for the higher moisture uptake capacity upon decreasing the AA/AMPS ratio can be attributed to the higher polarity of the sulfonic acid compared to the carboxylic acid. On the other hand, the increase can also be related to the higher amount of sulfonic acid groups being ionized at the same pH. Although this effect will be rather limited for DVS measurements, it will clearly be more pronounced in the swelling capacity.

3.5. Swelling capacity measurements on the synthesized SAPs

The swelling potential of the SAPs was determined in three swelling media (i.e. ultrapure water, demineralized water and cement filtrate solution). As such, a difference in the ionic concentration will result in a variation of the swelling capacity. On the other hand, the monomer ratio (AA/AMPS) will also have a strong influence on the swelling degree. Therefore, three samples with varying monomer ratio were selected for further testing including p(alg(1)_AA_{100}/$AMPS_0$(7)), p(alg(1)_AA_{50}/$AMPS_{50}$(7)) and p(alg(1)_AA_0/$AMPS_{100}$(7)). The results show (see Figure 4 (b)) that the swelling potential in cement filtrate is significantly ($p < 0.05$) lower, as anticipated due to the presence of Ca^{2+}, Mg^{2+} and other ions (Mignon et al., 2015b) as well as the lower osmotic pressure in a solution with a high ion concentration (Horkay, Tasaki & Basser, 2000). No significant differences could be observed between ultrapure water and demineralized water except for p(alg(1)_AA_0/$AMPS_{100}$(7)). Due to the high swelling of the latter, the relatively higher ion concentration of demineralized water resulted in a swelling reduction. An observed trend for the AA/AMPS ratio is that for all solutions, a decrease of the ratio leads to an increase of the swelling capacity, which is in excellent agreement with the obtained DVS results.

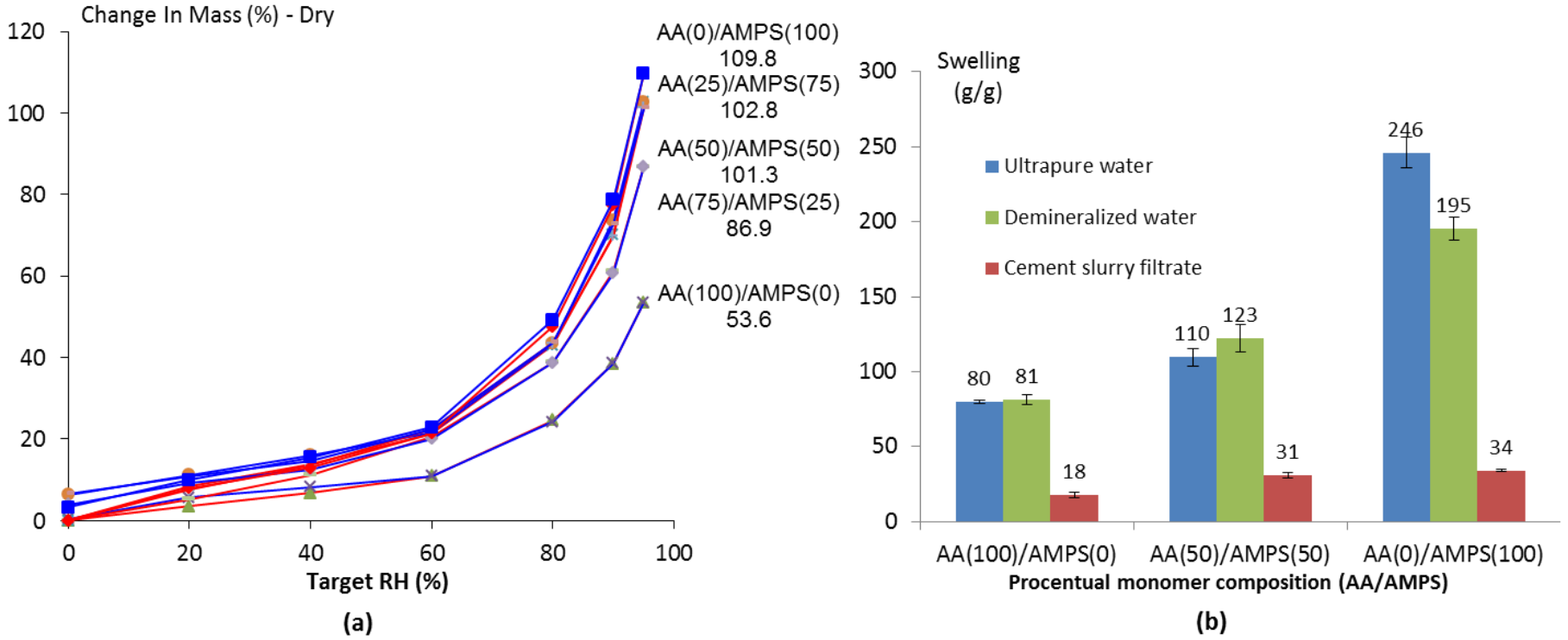

Figure 4: **(a)** Sorption and desorption isotherms of p(algMOD _AA/AMPS) materials measured by a Dynamic Vapor Sorption apparatus. The values underneed the sample names describe the maximal moisture uptake capacity (at 95% RH). **(b)** Swelling potential of the synthesized SAPs in ultrapure water, demineralized water and cement filtrate solution with a pH of 12.6. The samples are abbreviated by the molar ratio of the incorporated monomers according to: AA(x) /AMPS(y).

3.6. Thermal stability of the SAPs assessed by thermogravimetric analysis

The production of the SAPs occurs at 45°C while the temperature of concrete can rise up to 50 - 60°C during curing (Snoeck, 2015). Ideally, the polymers should not show thermal degradation at these temperatures. In order to study potential thermally induced degradation, TGA measurements were performed (see Figure 5). The results showed that at 100°C, over 90% of the material was maintained, while this loss can be attributed to residual water being present in the SAP as they were kept in the lab and no freeze drying step was performed right before the TGA measurements. Subsequently, the step at 200 – 250°C can be related to either the decarboxylation of the polymer and when AMPS is present the decomposition of sulfate groups. The last step around 360 – 450°C is the main chain C-C fission (Abdelaal, Makki & Sobahi, 2012; Diao et al., 2010).

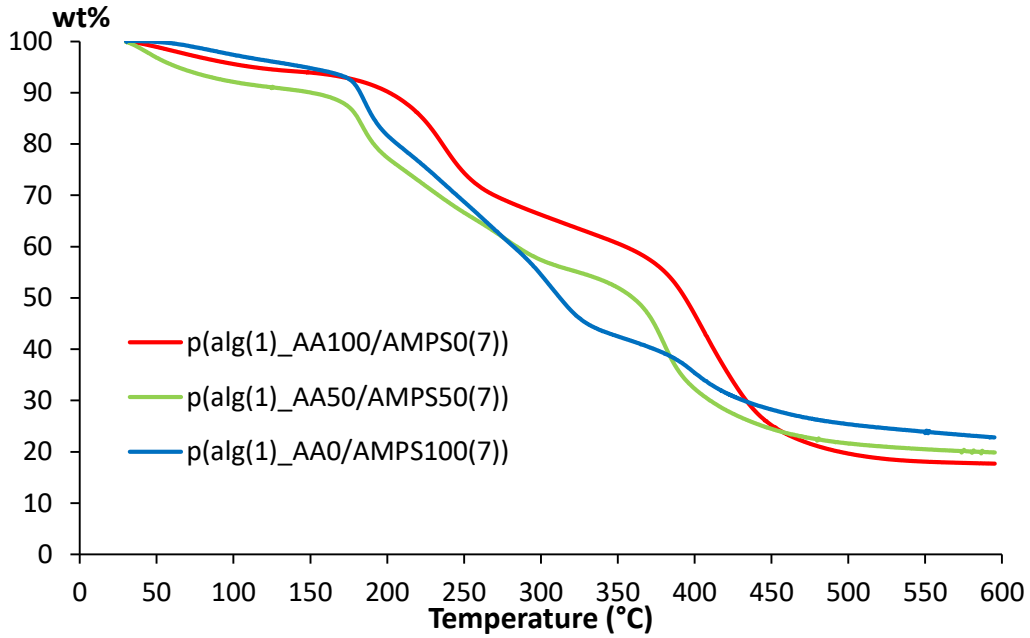

Figure 5: TGA plots displayed as the percentual weight as a function of temperature for p(alg(1)_AA_{100}/$AMPS_0$(7)), p(alg(1)_AA_{50}/$AMPS_{50}$(7)) and p(alg(1)_AA_0/$AMPS_{100}$(7)).

3.7. Effect of SAPs on the flexural and compressive strength of mortar samples

As the envisaged application includes their use in concrete, the SAPs were incorporated in mortar to investigate their effect on the flexural and compressive strength of the mortar samples. The composition of the mortar mixture is described in the materials and methods (chapter 2.11.)
Ideally, the SAPs should only exhibit a limited or no influence on the strength upon incorporating them in mortar. Interestingly (Table 3), p(alg(1)_AA_{100}/$AMPS_0$(7)) only results in a limited compressive strength reduction up to 7% upon addition of 1 wt% compared to the added amount of cement. This material can thus be considered extremely promising. The data indicate that SAPs with a higher molar fraction of AMPS lead to severely weaker mortar compared to the reference for both the bending and compressive strength, up to the point that they are not useful anymore for the envisaged application. Upon addition of 1 wt% p(alg(1)_AA_0/$AMPS_{100}$(7)) with respect to the added amount of cement, the matrix collapsed and was too weak to assess bending and compressive strength.

Table 3: Information on the additional water added on top of the 225g water initially, as well as the results of the three point bending and compression tests performed on the mortar samples containing 0.5 or 1 wt% p(alg(1)_AA_x/$AMPS_y$(7)).

Sample description	SAP concentration [w%]	Additional water [ml]	Bending strength [MPa]	Compressive strength [MPa]
Reference	0	0	7.6 ± 0.5	73.1 ± 1.6
p(alg(1)_AA_{100}/$AMPS_0$(7))	0.5	15	6.8 ± 0.4 (-11%)	68.9 ± 1.6 (-6%)
	1	30	7.6 ± 0.3 (/)	68.3 ± 0.6 (-7%)
p(alg(1)_AA_{50}/AM_{50}(7))	0.5	80	6.3 ± 0.4 (-17%)	42.1 ± 1.4 (-42%)
	1	150	5.1 ± 0.6 (-33%)	26.9 ± 0.2 (-63%)
p(alg(1)_AA_0/$AMPS_{100}$(7))	0.5	100	5.9 ± 0.3 (-22%)	36.6 ± 0.9 (-50%)

4. Conclusions and future perspectives

Alginate was successfully modified using methacrylic anhydride to create methacrylated alginate (algMOD) with a DS of 19% with respect to the hydroxyl groups present. ATR-IR and HR-MAS ^{1}H-NMR spectroscopy enabled to confirm the SAP structure as well as the cross-linking efficiency. The materials possessed gel fractions ranging between 43 and 85%, which decreased upon decreasing the AA/AMPS molar ratio. The SAPs showed a moisture uptake capacity going from 54 to 110% their own weight at a RH of 95% upon increasing the AMPS ratio. Interestingly, all materials showed a negligible hysteresis which implies that they can be used as a reservoir and all moisture taken up will also be completely desorbed again. When investigating the swelling capacity, it was observed that an increase of the AMPS content led to an increased swelling, independent of the used solution, up to a maximal swelling potential of 246 times its own weight for p(alg(1)_AA_0/$AMPS_{100}$(7)) in ultrapure water. Additionally, these polymers showed a thermal stability above 100°C, indicating that they will not degrade during the curing of the concrete matrix. After incorporation of the SAPs in mortar, it was determined that a decrease of the AA/AMPS ratio resulted in a severe decrease of the compressive strength of mortar. Interestingly, p(alg(1)_AA_{100}/$AMPS_0$(7)) showed only a very limited decrease in compressive strength (up to 7% decrease upon addition of 1 wt% SAP). Despite the rather limited moisture uptake and swelling capacity, this latter material showed the highest gel fractions and very limited effect on the compressive strength, rendering this material very interesting for the envisaged application. This material will thus be further tested for its self-sealing and -healing potential. The latter will be the topic of a forthcoming paper.

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