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Combinatory approach of methacrylated alginate and acid monomers for concrete applications

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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.

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, 2006), frost resistance (Jensen, 2013; Laustsen, Hasholt, & Jensen, 2013) and self-sealing and -healing of cracks (Mignon, Graulus et al., 2015; 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, Graulus et al., 2015; Mignon, Snoeck et al., 2015; Snoeck, Van Tittelboom et al., 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 et al., 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 et al., 2014; Snoeck, Van Tittelboom et al., 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

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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 and Zohuriaan-Mehr, 2008; Nesrinne & Djamel, 2013; Zhang et al., 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 h after the addition of MAAH. Afterwards, dialysis (12–14 kDa) was performed for 72 h 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 h, the gel fraction could be determined using the following equation:

$$G\,[\%] = {}^{W}\!/_{W_0} \tag{1}$$

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, Graulus et al., 2015) with systematic steps of 20, 40, 60, 80, 90 and 95% RH.

2.3.1. Swelling tests performed in ultrapure and demineralized water

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 3 h 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 Eq. (2):

$$\textit{Swelling capacity} = {}^{\left(m_0 - m_{filter}\right)}\!/_{m_{SAP}} \tag{2}$$