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Development of amine-based pH-responsive superabsorbent polymers for mortar applications

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HIGHLIGHTS

- pH-responsive superabsorbent polymers has been successfully synthesized.
- They showed a desired pH-responsive swelling behavior (up to 70 times their weight).
- No degree of hydrolysis is observed after swelling in alkaline solutions.
- Only a limited compressive strength reduction of mortar is observed.
- Using 'smart' pH-responsive SAPs could be promising for self-healing concrete.

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ABSTRACT

Superabsorbent polymers (SAPs) have already found their way in many applications. Some of these polymers undergo major characteristic changes by small environmental variations which makes them interesting for self-healing of cracks in concrete. In the present work, polymer networks composed of dimethylaminoethyl methacrylate and *N*,*N*′-methylenebisacrylamide have been synthesized. Moisture uptake capacities up to 45% were measured at a relative humidity of 95%. They showed a desired pH-responsive swelling behavior with no degree of degradation. A small significant mortar strength reduction is found with addition up to 1 m% compared to the cement mass. All results were compared to commercially available SAPs.

1. Introduction

Cracking is a major concern in building applications, which can be tackled by limiting the crack width, creating moist environmental conditions and improving hydration and crystallization [1]. Particularly interesting in this respect is the use of superabsorbent polymers (SAPs) which are materials that enable to absorb up to 500 times their own weight in water [2]. SAPs can be added to concrete during the mixing process and can be used next to self-healing of cracks for other applications such as freeze/thaw resistance [3–7]. According to different authors [5,8,9], there exists a link between freeze/thaw resistance and internal curing. As the SAPs will release their water during hardening, they will leave behind air-filled pores. During freeze/thaw cycles, these voids can protect concrete in a similar way as by using air entrainment.

Now regarding self-healing applications, when a crevice is exposed to the environment, water will ingress that can be absorbed by the incorporated SAPs. As a result, they seal the crack from intruding fluids and gases, which can negatively influence the structure durability [10]. Additionally, the swelling of the SAPs may result in overall water-tightness, thereby promoting autogenous healing.

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Previous research has already elaborated on the application of a series of synthetic SAPs based on acrylic acid and acrylamide [11,12]. Interestingly, upon addition of 1 m% (with respect to the cement present) SAPs, a strong sealing capacity has already been realized as indicated by water permeability tests. However, these SAPs already show strong swelling during mixing and release a large part of the entrained water due to a decrease in relative humidity during cement hydration. On the one hand, the latter promotes internal curing which aids in maintaining the internal relative humidity of the concrete matrix [13]. On the other hand, by releasing this water, the SAPs shrink resulting in the formation of macro-pores which negatively influence the concrete strength [12,14]. Due to the required SAP amount (up to 1 m%) for the targeted application, the negative effect on the concrete strength was more pronounced [15,16]. The current manuscript aims to overcome the latter drawback through the application of pH-responsive SAPs.

Some SAPs can be triggered by external stimuli [17] such as pH [18,19], temperature [20,21], pressure [22] or light [23]. They exhibit a strong difference in swelling potential upon minimally varying these stimuli.

pH-responsive SAPs could thus potentially solve the issue of a severe decrease in mortar strength associated with the application of conventional SAPs. Indeed, by using a basic monomer such as dimethylaminoethyl methacrylate (DMAEMA), the resulting SAP would on the one hand not swell substantially upon exposure to a pH above its pKa value of 8.4 [24] where the amine moieties will not be protonated. The pH of fresh mortar is very alkaline, pH 12.5–13, as such a low swelling degree at an alkaline pH will lead to smaller macro pores. On the other hand, when water infiltrates a crack, the SAP will swell more given the more neutral pH of the infiltrating water (i.e. pH 7–9). This is explained more graphically in Fig. 1.

Poly(DMAEMA) has already been used as a copolymer combined with *N*-isopropylacrylamide (NIPAAm) to create hydrogels with both pH- as well as temperature sensitivity [26]. Another study reported on the application of NIPAAm, acrylic acid (AA) and DMAEMA as starting monomers for the development of a multi-responsive adaptive liquid microlens [27]. Other researchers have shown the potential of grafting p(DMAEMA) from a poly(thiophene) backbone to create a reversible pH-response in different aqueous solutions rendering it attractive for fabricating functional polymer composites [28]. A copolymer of hydroxyethyl methacrylate (HEMA) and DMAEMA has even been reported as a sensor for CO_2-detection [29].

As p(DMAEMA) has already shown its potential for a plethora of applications, it can also be beneficial to investigate its effect for the self-sealing and -healing of cracks in concrete. In the present work, DMAEMA will be cross-linked with the synthetic bifunctional cross-linker *N*,*N*′-methylene bisacrylamide (MBA). First, the chemical structure of the synthesized SAPs will be elucidated by attenuated total reflectance-infrared (ATR-IR) spectroscopy while its cross-linking efficiency will be assessed by high-resolution magic angle spinning proton nuclear magnetic resonance (HR-MAS ^{1}H NMR) spectroscopy. The moisture uptake capacity will be evaluated by dynamic vapor sorption (DVS) measurements while the pH-responsiveness of cross-linked poly(dimethylaminoethyl methacrylate) (p(DMAEMA)_x) will be identified by swelling capacity tests in aqueous solutions of a varying pH as well as in a cement filtrate (CF) solution. Finally, the effect of the SAPs upon incorporation in mortar will be identified by flexural and compressive strength tests. The latter will provide an indication of their potential for the envisaged self-healing application, as compared to commercially available synthetic SAPs [30].

2. Materials and methods

2.1. Materials

Ammonium persulfate (APS) and dimethylaminoethyl methacrylate (DMAEMA) come from Sigma-Aldrich (Bornem, Belgium). *N*,*N*′-methylene bisacrylamide (MBA) was purchased at Merck (Nottingham, UK). *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine (TEMED) was bought at Acros Organics (Geel, Belgium). The paper filters (retention of 8–12 μm) originate from Munktell filters (Bärenstein, Germany). Commercial SAP A is a copolymer of acrylamide and sodium acrylate and commercial SAP B is a cross-linked potassium salt poly(acrylate). Both come from BASF (BASF Construction Chemicals GmbH, Trostberg, Germany) and were synthesized via bulk polymerization.

2.2. Synthesis of cross-linked p(DMAEMA)

The SAPs were synthesized by combining dimethylaminoethyl methacrylate (DMAEMA) with the bifunctional cross-linker *N*,*N*′-methylene bisacrylamide (MBA) in altering molar fractions (2 and 4 mol% as a function of the total amount of added DMAEMA). Next, the redox initiator pair ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TEMED) was added. APS was mixed in at a concentration of 2 m% (corresponding to 1.4 and 1.1 mol% respectively for 2 and 4 mol% MBA) with respect to the total combined weight of the monomers and cross-linker. TEMED was then added in a 1/1 vol% (corresponding to 0.8/1 and 1/1 mol% respectively) ratio with APS. Water was used as a solvent (250 g monomers and cross-linker/L) in a three-neck flask. To avoid inhibition of the reaction by oxygen, the system was put under nitrogen (N_2) atmosphere. APS was added after flushing by using a syringe through a septum. The reaction was executed at an elevated temperature of 45 °C while stirring continuously. The reaction mechanism is schematically represented in Fig. 2. After 24 h, the SAP was removed from the flask and purified by incubation in water for another 24 h. Finally, the product was lyophilized by means of a Christ freeze-dryer alpha 2–4-LSC and grinded into a fine powder during 20 s with an A11 basic Analytical Mill which has a motor rating input of 160 W and maximal speed of 28,000 rpm.

2.3. Gel fraction assessment

Dialysis was used to remove any remaining unreacted particles after polymerization. The ratio of the dry weights of the sample before and after purification for 24 h will determine the gel fraction:

$$G\ [\%] = W/W_0 \quad (1)$$

W equals the weight of the dry insoluble part of the sample.
W_0 equals the initial dry weight of the sample.

2.4. Particle size distribution obtained via optical microscopy

The particle size diameter was determined by a Zeiss Axiotech optical microscope in combination with the digital image capturing software ZEN core and the analysing software ImageJ. A sample population >100 has been used.

2.5. Attenuated total reflectance Fourier transform infrared spectroscopy

A PerkinElmer Frontier FT-IR (midIR) combined with a MKII Golden Gate set-up equipped with a diamond crystal from Specac