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pH-responsive superabsorbent polymers: A pathway to self-healing of mortar

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ABSTRACT

Cracks are concrete's worst problem. External, passive treatments are expensive and time consuming. pH-responsive superabsorbent polymers (SAPs) offer an internal active solution. When cracks occur, the SAPs can swell, fill the crack (self-sealing) and assist in the formation of healing products (self-healing). In previous work, a range of (superabsorbent) polymers have been synthesized and characterized. Based on these results, the two best performing SAPs were chosen for further characterization. The results indicate that the SAPs developed do not show degradation in cement filtrate solutions. Upon addition of SAPs, a decrease in mortar strength occurred, yet a positive effect on self-sealing was observed since the water permeability decreased. Furthermore, the formation of products became apparent at the sealed cracks of the mortar samples containing 1 m% SAPs. Identification using scanning electron microscopy, infrared spectroscopy and thermogravimetric analysis indicated that the products mainly consisted of healing products (more specifically $CaCO_3$) which is illustrative for self-healing.

1. Introduction

Concrete is the most important building material, due to its ease to use and relatively low cost compared to other construction materials. Worldwide, over 10 billion tons are produced annually [1]. Concrete has high mechanical and durability properties. On the other hand, it has a relatively low tensile strength. For that reason, concrete is nearly always reinforced with steel bars to bear the tensile loads. These conditions make crack formation one of the largest issues in concrete applications. High tensile stresses can, among other, be the result of external loads, imposed deformations and expansive reactions [2]. The presence of cracks endangers the durability of concrete and can lead to corrosion of the reinforcement, since a pathway for harmful particles dissolved in fluids and gases is generated [3]. Maintenance and repair thus becomes unavoidable. For crack repair, a variety of external techniques are available including manual repair with epoxy [4], polyurethane [2,5], coating the concrete surface by electrodeposition of chemical compounds [6], etc. These solutions are expensive, time-consuming and in some cases, visually unattractive. Restoration costs can exceed half of the annual construction budget [7]. If cracks are formed in inaccessible places, manual repair even becomes impossible.

Throughout the last decades, great advances have arisen in concrete repair technology. As such, instead of an external, passive and expensive treatment, an internal and active treatment can offer a superior solution. Self-healing materials have the ability to reverse the damage development once or multiple times and aid in expanding the lifetime and reliability of the concrete (i.e. the so-called 'damage management concept') [8]. Cracks would be able to seal and heal automatically, similar to broken bones and damaged skin or tissue that is able to regenerate.

Concrete as such shows a sort of self-healing (i.e. autogenous healing) [9,10]. As water enters the crack, unhydrated cement particles, which are still present in the concrete matrix, will be hydrated and new calcium silicate hydrate (C–S–H) will form together with the preposition of calcium carbonate for blocking the crack [11]. This will aid in healing small cracks completely up to 30–50 μm and partially up to 150 μm [12,13] in strain-hardening cementitious materials. The width of crack closure depends on the surrounding conditions and composition [14]. However, in case of larger cracks, autogenous healing will not be sufficient for full crack repair. An alternative solution for the healing of larger cracks is important to avoid the increase of maintenance costs.

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In the present article, an internal and active self-healing treatment is examined by the incorporation of superabsorbent polymers (SAPs) during the mixing process. Superabsorbent polymer materials are cross-linked polymer networks able to swell in solution. There exists a wide range of developed SAPs. As discussed earlier [15], some SAPs can undergo large changes in swelling capacity upon small environmental variations (i.e. 'smart' polymers). The use of pH-responsive SAPs can be extremely useful for the targeted application of self-sealing and self-healing. When cracks in concrete are subjected to external wetting, ingress of moisture will cause the SAP to swell. When the external fluid possesses a low ionic concentration, the SAP swells to such an extent that it completely fills the crack and slow down or even prevent the further infiltration of water. In addition, these polymers may promote the autogenous healing and help retain the water-tightness of cracked concrete constructions [16,17]. As cracks are exposed to a varying pH depending on the surrounding conditions, the swelling capacity of these SAPs and the release of water inside concrete can be controlled.

In previous work, a range of (superabsorbent) polymers composed of acrylic acid, acrylamide and methylene bisacrylamide as cross-linker has already been synthesized and characterized. Based on the envisaged application, the two superior SAPs were chosen for further characterization. The influence of SAP introduction on the strength and the self-sealing and -healing of mortar is also evaluated herein. First, the SAPs are characterized by comparing their swelling capacity at varying pH-values in aqueous solutions and (acidified) cement filtrate. In a second part, the mechanical properties of mortar mixtures in the absence and presence of SAPs are compared by performing flexural and compressive tests. The sealing efficiency and the potential for self-healing are subsequently measured through a water permeability set-up. The goal of this article is thus to elucidate the effect of a variation in the chemical composition of the SAPs (especially with respect to the monomer ratio) on the strength and the self-sealing of cracks in mortar. Commercially available SAPs have a fixed composition which is often even not fully elucidated. For that reason, a comparison between the synthesized and commercially available SAPs is useful and necessary. Additionally, the novelty in this article lies in a study on possible degradation of the SAP inside mortar. Moreover, in contrast to conventionally applied analysis techniques to evaluate self-healing, the present work will also include a full structural characterization of potential healing products generated during the water permeability assays using among other scanning electron microscopy energy-dispersive spectroscopy, infrared spectroscopy and thermogravimetric analysis.

2. Materials and methods

2.1. Materials

The SAPs were in-house synthesized in an inert N_2-atmosphere at 45 °C. The synthesis has already been explained in a previous paper [15]. All chemicals were used as received, unless otherwise stated. Acrylic acid (AA, 99.5%), N,N,N′,N′-tetramethylethylene diamine (TEMED, 99%) and hydrochloric acid (HCl, 37% in water) were purchased from Acros Organics (Geel, Belgium). Acrylamide (AM, 99+%) was obtained from Janssen Chimica (Geel, Belgium). N,N′-methylene bisacrylamide (MBA, 99%) was purchased at Merck (Nottingham, UK). Ammonium persulfate (APS, 98+%) and sodium hydroxide (NaOH, 97%) were obtained from Sigma-Aldrich Fine Chemicals (Bornem, Belgium). The used filters for measuring the swelling capacity were purchased from Munktell filters and showed a typical retention of 8–12 μm (Bärenstein, Germany). The studied mortar mixtures were composed of Ordinary Portland Cement (OPC, CEM I 52.5 N; 510 kg/m^3) and silica sand 0/2 (1530 kg/m^3) for a mixture without SAPs. A water to cement ratio (W/C) of 0.5 was used and a varying amount of SAPs expressed as SAP/C (dosage of superabsorbent polymer by weight per mass unit of cement: 0.005 and 0.01) with additional water added to realize the same workability as the reference samples. The swelling capacity in cement filtrate (see Section 2.2) provides a good indication of the required amount of additional water in mortar. In the framework of the strength tests, additional mortar samples were made with a polycarboxylate superplasticizer (Glenium 51, conc. 35%) instead of additional water to study the influence of additional water and amount of superplasticizer on the mechanical properties.

2.2. Swelling studies in (acidified) cement filtrate

The swelling capacity of the SAPs was measured as the mass change between the freeze-dried and the swollen (i.e. saturated) state of the particles. A mass of 0.20 g polymer was mixed with 100 mL of a solution of (acidified) cement filtrate (CF). The CF was made by mixing10 g OPC and 100 mL demineralized water for 3 h with a mechanical stirrer, followed by filtration to remove the cement particles and collecting the solution. HCl was added if required to adjust the pH to the targeted values (pH 9–12). An additional measurement was performed in triplicate at pH 13 by the addition of NaOH. This is useful to have a better understanding of the swelling effect at that extreme basic condition. After 24 h, a filter was used to collect the remaining water that is not absorbed by the SAPs. By calculating the mass 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. (1):

$$\text{swelling capacity} = (m_0 - m_{\text{filtered}})/m_{\text{SAP}} \quad (1)$$

in which m_0 is the initially added water mass [g], m_{filtered} 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 filtration to exclude its influence on the mass of the filtered water. All standard deviations reported were for single values and have been calculated based on three measurements. The results in (acidified) cement filtrate were herein compared with our previously reported swelling capacity measurements performed on the two selected SAPs in aqueous solutions with varying pH-values (pH 1–13) [15]. These 2 SAPs were selected on their superabsorbent behavior and are thus further characterized herein.

2.3. Infrared measurements on dried SAPs (after swelling)

A PerkinElmer Frontier FT-IR (midIR) combined with a MKII Golden Gate set-up equipped with a diamond crystal from Specac was used to determine the chemical composition of the SAPs, prior to and after performing swelling experiments. The results were analyzed with the PerkinElmer Spectrum Analysis software.

2.4. Mixing procedure

First, the cement and SAP were mixed together using a standard mortar mixer. Water was brought into contact with the dry mixture and mixed at 140 rpm for 30 s. The sand was steadily added during the next 30 s with the same rotational speed. The mixer was brought to a high speed (285 rpm) for an additional 30 s. The mixing was subsequently stopped for 90 s. The first 30 s, the mortar was scraped from the bowl and then left resting for 60 s. Afterwards, the mixing was continued for 60 s at high speed, following the method described in EN 196-1. The workability was measured by means of a jolting table as described in EN 12350-5. The samples were then molded as described in EN 196-1. The resulting materials were stored in a climate room with a relative humidity of 95 ± 5% and a temperature of 20 ± 2 °C for 28 days.

2.5. Bending and compression tests

Flexural and compressive strength were measured by means of a three-point-bending test on 160 × 40 × 40 mm^3 mortar beams (at an