Smart superabsorbent polymers for self-sealing and -healing of mortar

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Abstract: Concrete is an important building material, due to its ease to use and relatively low cost. However, the presence of cracks endangers the durability of concrete and can result in reinforcement corrosion since a pathway for harmful particles dissolved in fluids and gases is generated. Manual repair costs can go up to half of the annual construction budget. Instead, introducing a superabsorbent polymer (SAP) during concrete mixing can create a self-sealing and -healing material.

Some SAPs undergo major characteristic changes by small environmental variations. These so-called ‘smart’ polymers have the ability to sense environmental stimuli. The use of pH-responsive SAPs can be extremely useful for the envisaged application (i.e. self-sealing and self-healing of cracks). 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 strength, the SAP will swell 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 autogenous healing.

The proposed paper discusses the self-sealing and -healing effect of two pH-responsive SAPs. First, the SAPs have been characterized completely. They are inserted in mortar (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). The sealing efficiency has been measured through a water permeability set-up. The results indicate that a higher fraction of SAP leads to a stronger self-sealing. Interestingly, the formation of the healing products is found at the bottom of the cracks after the water permeability measurements, indicating the self-healing effect of these SAPs. These newly developed polymers are thus promising for the targeted application.

1. INTRODUCTION

Concrete is the most important building material, due to its ease to use and relatively low cost compared to other construction materials. Concrete exhibits good mechanical properties. On the other hand, it shows a relatively low tensile strength. These conditions make crack formation one of the largest issues in concrete applications. 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. Maintenance and repair thus becomes unavoidable. External, passive solutions are expensive, time-consuming and in some cases, visually unattractive. Restoration costs can exceed half of the annual construction budget [1]. 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, several or multiple times and aid in expanding the lifetime and reliability of the concrete (i.e. the so-called ‘damage management concept’) [2]. In the present article, an internal and active self-healing treatment is examined by the incorporation of superabsorbent polymers (SAPs) during the mixing process.

SAPs are cross-linked hydrogel networks consisting of water-soluble polymers. Interestingly, these hydrophilic superabsorbent networks can take up aqueous solutions to several hundred times their own weight [3, 4]. Some SAPs can undergo large changes in swelling capacity upon small environmental variations. 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 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. 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.

2. MATERIALS AND METHODS

The SAPs were in-house synthesized in an inert N_2-atmosphere at 45 °C. The synthesis has already been described in a previous paper [5]. All chemicals were used as received, unless otherwise stated. Acrylic acid (AA), N,N,N’,N’- tetramethylethylene diamine (TEMED) and hydrochloric acid (HCl) were purchased from Acros Organics (Geel, Belgium). Acrylamide (AM) was obtained from Janssen Chimica (Geel, Belgium). N,N’-methylene bisacrylamide (MBA) was purchased at Merck (Nottingham, UK). Ammonium persulfate (APS) and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich Fine Chemicals (Bornem, Belgium). 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 was added on top to receive the same workability as the reference samples.

Permeability tests were performed, starting at an age of 28 days after cracking cylindrical specimens at the age of 14 days by means of a crack width-controlled splitting test (Walter + Bai DB 250/15). The dimensions of the cylindrical samples used in the permeability tests were 78 mm in diameter and 20 mm in height. The crack width was controlled during the splitting test with two linear variable difference transducers (LVDTs) (Solartron AX/0.5/S; Solartron Metrology, West Sussex, UK; with an accuracy of 1 µm). The residual crack widths ranged between 150 – 245 µm. After splitting, the samples were taped at the sides to avoid the entrance of epoxy at the sides of the crack and glued with epoxy into a poly(vinylchloride) (PVC) tube to exclude side effects during the permeability tests and to receive unidirectional water flow. The samples were vacuum-saturated with water and placed into the water permeability test setup at an age of 28 days.

The self-sealing efficiency was measured as the decrease in water flow through the crack over time. Starting from Darcy’s law, an expression for the coefficient of water permeability k (m/s) is found using equation (1):

$$k = (a \cdot L) / (A \cdot t_f) \cdot \ln(h_0 / h_f) \qquad (1)$$

in which a is the cross-sectional area of the fluid column [m^2], L is the thickness of the specimen [m], A represents the surface area of the sample subjected to the flow [m^2], t_f is the measured time [s], h_0 is the initial pressure head [m] and h_f represents the remaining pressure head [m].

Permeability readings for all specimens were collected every day during 28 days. During the measurements, the specimens remained completely submerged. On the 28th day (at an age of 56 days), the average coefficients of water permeability of the samples were compared.

Univariate ANOVA tests with two factors, followed by a Tukey post-hoc test were performed in the statistical program SPSS to identify significant differences. All standard deviations reported were for single values and have been calculated based on three measurements or more to ensure statistically relevant results.

3. RESULTS AND DISCUSSION

Water permeability measurements indicate the self-sealing effect of SAPs present inside cylindrical mortar samples. Figure 1 shows water permeability measurements in the presence of a variable amount and type of SAP, compared to the reference samples.

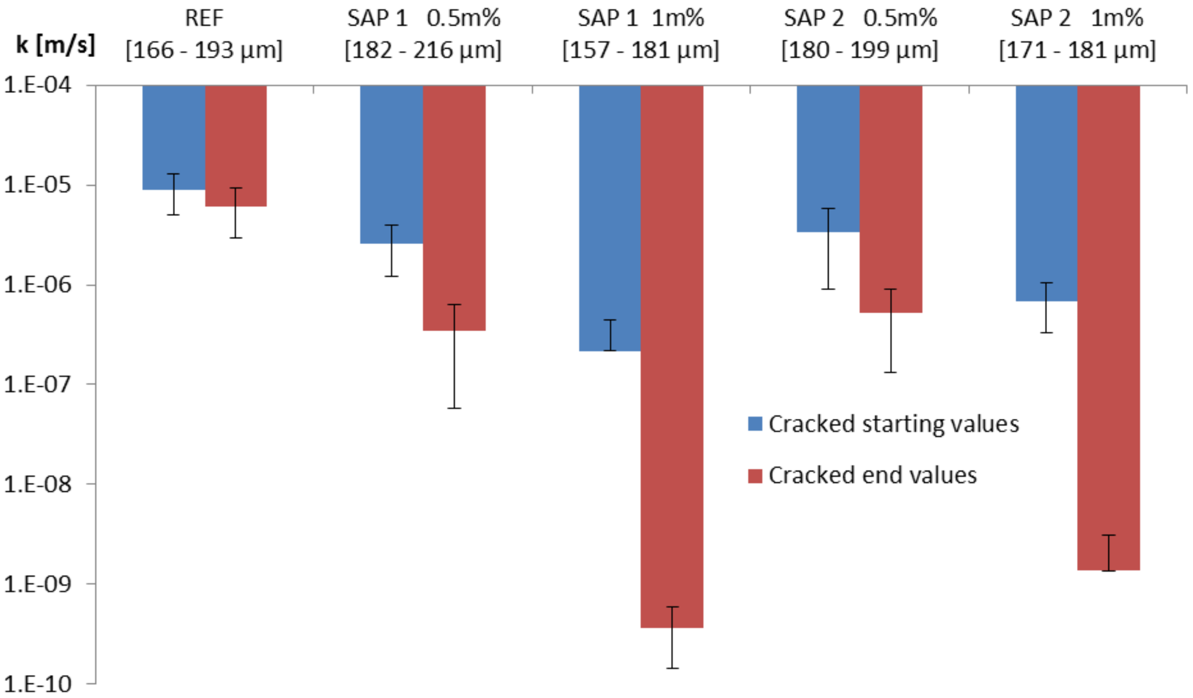

Figure 1: Water permeability measurements performed on mortars with and without SAPs. The range of the crack widths is shown between brackets.

As anticipated, cracked reference samples do not show significant sealing when comparing the starting and end values. Interestingly, upon addition of any amount or type of the synthesized pH-sensitive SAPs, a significant ($p < 0.05$, addition of 0.5 m% SAP) or a very significant ($p < 0.01$, addition of 1 m% SAP) closure of the cracks is observed after 28 days. When comparing the added amounts of SAPs, independent of the SAP type applied, the cracked samples containing 0.5 m% SAP do not result in a significant difference with the reference sample at the onset of the measurements (at the age of 28 days, starting value), but results in a significant difference at the end of the measurements (at the age of 56 days, end value). The latter implies that even 0.5 m% SAP results in a stronger sealing effect over a period of 28 days compared to autogenous healing of the reference samples.

As anticipated, addition of 1 m% SAP results in better closure compared to the reference and the samples containing 0.5 m% SAP. More SAP equals a higher swelling capacity and as such, a stronger blockage of the cracks and potential to stimulate further cement hydration and $CaCO_3$ precipitation.

Interestingly, stalactites have been observed after performing water permeability tests on samples containing 1 m% SAP as seen in Figure 2. In-depth characterization confirms the formation of the main healing product $CaCO_3$ which leached out from the crack (data not shown).

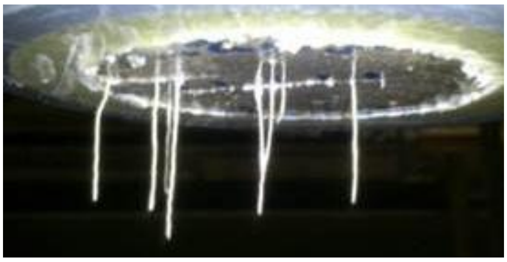

Figure 2: Stalactite formation at the bottom of the water permeability samples upon addition of 1 m% of the pH-responsive SAP.

4. CONCLUSION

The addition of any amount of SAP to mortar leads to a significantly stronger sealing effect of cracks over a period of 28 days compared to reference mortars without SAPs. The addition of higher amounts of SAPs (up to 1 m%) results in a superior self-sealing effect. Interestingly, stalactites have been observed on samples containing 1 m% SAP. In-depth characterization showed that the main healing products was $CaCO_3$ (with small fractions of CaO). This supports the strong self-sealing and self-healing capacity of cracks upon addition of 1 m% of the synthesized SAPs inside mortar.

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