



Alginate biopolymers: Counteracting the impact of superabsorbent polymers on mortar strength



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HIGHLIGHTS

- CaAlg exhibits a strong moisture uptake capacity especially at air RH.
- NaAlg becomes insoluble in mortar due to the divalent cations present in CF.
- CaAlg leads to only a small compression strength reduction <15% upon 1 m% addition.
- All alginates except NaAlg 1 m% meet the strength demand of 52.5 MPa at 28 days.
- Alginate can be considered a very promising material in concrete applications.

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ABSTRACT

Synthetic superabsorbent polymers (SAPs) are used in concrete for various applications. However, the addition of SAPs may lead to a significant decrease in mortar strength. In order to overcome this bottleneck, the present work focuses on the application of biopolymers as SAPs, more specifically polysaccharides including both uncross-linked sodium alginate as well as physically cross-linked calcium alginate. Interestingly, results indicate no or a limited (i.e. < 15%) reduction in strength upon introducing 1% relative to cement mass. Alginate can therefore be considered a promising material, not only for internal curing but even when high SAP amounts are required.

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1. Introduction

Concrete is worldwide the most often used building material which shows excellent mechanical and durability properties.

Abbreviations: DVS, dynamic vapor sorption; SAP, superabsorbent polymer; NaAlg, sodium alginate; CaAlg, calcium alginate; C-S-H, calcium silicate hydrates; CaCl₂, calcium chloride; RH, relative humidity; CF, cement filtrate.

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Nevertheless, its relatively low tensile strength leads to the presence of cracks. The presence of wide cracks, which accelerates ingress of harmful substances, can lead to corrosion of the reinforcements as a pathway for harmful substances dissolved in fluids and gases is generated [1]. However, concrete as such exhibits a passive healing capacity (i.e. autogenous healing) [2,3]. In a hardened cementitious matrix, unhydrated cement particles remain present. Water entering the cracks results in a continued hydration of these unhydrated grains and the formation of calcium silicate hydrates (C-S-H) together with the deposition of calcium carbonate crystals [4]. The latter can result in the healing of small cracks (complete healing up to 30–50 μm and partially up to 150 μm [5,6] in strain-hardening cementitious materials).

Wider cracks cannot be repaired completely by means of autogenous healing. External techniques such as manual repair with epoxy [7] are used nowadays. This manual repair is however expensive, time-consuming and visually unattractive. If cracks are formed in inaccessible places, manual repair even becomes impossible. Instead of an external and expensive treatment, an incorporated smart treatment that is activated when needed, provides a superior solution as the cracks would seal and heal automatically, without any need for an additional external intervention.

The use of superabsorbent polymers (SAPs) may provide such a smart internal solution. SAPs are cross-linked polymer networks able to take up aqueous solutions up to several hundred times their own weight [8,9]. Nowadays, reports have already been presented in literature regarding synthetic SAPs used in concrete for various applications such as internal curing [10,11], frost resistance [12,13] and crack-sealing and -healing [6,14,15]. However, these 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 [12,16,17]. As for self-sealing [18] and self-healing applications [14,17] high SAP amounts are required (up to 1% relative to cement mass), the macropore formation becomes more critical especially when high amounts of additional water are used to compensate for the loss in workability.

In the present work, the potential of a novel biopolymer (i.e. alginate) is evaluated to realize self-sealing and -healing of cracks. The structural integrity of mortar is investigated. In addition to its low cost, it might also contribute to a sustainable approach for concrete repair through natural materials.

Sodium alginate is a water-soluble anionic polysaccharide extracted from the cell walls of brown algae. It is a linear copolymer composed of mannuronic and guluronic acid, covalently linked in varying sequences and blocks and is commercially available as a sodium salt (NaAlg). Interestingly, when NaAlg is combined with multivalent cations such as calcium (originating from salts such as calcium chloride, CaCl_2), a physically cross-linked network is formed, which becomes insoluble in water.

To the best of our knowledge, alginate has only been reported scarcely so far in combination with concrete. It is reported that alginate can form gels on contact with cementitious materials and can be assessed for their ability to protect encapsulated microorganisms (*Sporosarcina pasteurii*). However, they are not used as the main healing agent as the healing procedure relies on bacteria-induced self-healing [19]. Similarly, in our earlier research we have incorporated ureolytic bacteria in a cross-linked Pluronic F-127 bismethacrylate hydrogel to realize a smart, two-step self-healing approach [19,20]. However, a severe effect on the strength was observed, so a need for a superior hydrogel is necessary.

The present work aims to evaluate the potential of both NaAlg as well as physically cross-linked CaAlg as SAPs to establish a sustainable approach towards self-sealing and -healing concrete without impairing mechanical strength. To this end, (cross-linked) alginate will herein be characterized by first using dynamic vapor sorption measurements to determine the moisture uptake capacity. Subsequently, the swelling properties in both demineralized water as well as in cement filtrate solution are tested. In a final part, the mechanical properties of mortar mixtures in the absence

and in the presence of SAPs are examined by performing flexural and compressive tests. All properties are compared with those earlier obtained using commercially available synthetic SAPs from BASF [21]. The results of the alginates are anticipated to provide an indication of the applicability of biopolymers in the field of self-sealing and self-healing concrete and will therefore assist in guiding future research in the field.

2. Materials and methods

2.1. Materials

Sodium alginate (NaAlg) and hydrogen peroxide were purchased from Sigma-Aldrich Fine Chemicals (Bornem, Belgium). Calcium chloride (CaCl_2) was obtained from Acros Organics (Geel, Belgium). Nitric acid (HNO_3) was of analytical grade (ChemLab, Belgium). Two types of SAPs from the company BASF (BASF Construction Chemicals GmbH, Trostberg, Germany) were used for comparison. These include SAP A, a copolymer of acrylamide and sodium acrylate, and SAP B, a cross-linked potassium salt polyacrylate. The studied mortar mixtures (following EN 196-1, 450 g cement + 225 g water + 1350 g sand) 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 polymers. A water to cement ratio (W/C) of 0.5 was used as an equal W/C ratio has already been used in earlier research using synthetic SAPs [17,22]. Indeed, the latter comparison enables to elucidate if and to what extent the alginates outperform the synthetic SAPs applied before. A varying amount of alginate expressed as Alg/C (dosage of NaAlg or CaAlg by weight per mass unit of cement: 0.005 and 0.01) with additional water was added to obtain the same workability compared to the reference samples.

2.2. Hydrogel formation

For the development of CaAlg, a CaCl_2 (100 mM) and a 1 w/v% NaAlg aqueous solution were prepared. By slowly adding the NaAlg solution drop-wise in the CaCl_2 , CaAlg beads are formed which can easily be separated from the solution through filtration. Finally, the product was lyophilized by means of a Christ freeze-dryer alpha 2-4-LSC. The chemical structure of both alginates is shown in Fig. 1. Over 95% of the obtained particle sizes range from 2 to 85 μm for NaAlg and from 2 to 101 μm for CaAlg.

2.3. Dynamic vapor sorption (DVS) measurements

DVS measurements were applied to determine the moisture uptake capacity at different relative humidities (RH). The equipment consists of a Cahn microbalance, a temperature-controlled housing and mass flow controllers which control the appropriate flow of the wet and dry N_2 gas. The benefit of this technique is the control over both the relative humidity as well as the temperature (i.e. 21 °C). For the DVS analysis, approximately 5–10 mg of freeze-dried SAP was placed in the sample pan. A first step (RH of 0%) was necessary to start with a completely dry material. Afterwards, the humidity was varied in systematic steps (i.e. 20, 40, 60, 70, 80, 90 and 98%). Every subsequent step was initiated when the change of the sample mass as a function of time was lower than 0.02 mg/min. After an equilibrium value was obtained at the highest RH (98%), desorption was realized in consecutive RH steps similar to the sorption process until full desorption. If required, the equilibrium values were computed from the weight versus time curves by extrapolation using the exponential function presented in Eq. (1):

$$m(t) = a \cdot (1 - b \cdot \exp(-c \cdot t)) \quad (1)$$

where $m(t)$ is the mass of the sample at time t , while the coefficients a , b and c can be determined by means of non-linear curve fitting.

2.4. Swelling studies

The swelling capacity of the polymers was measured as the mass change between the freeze-dried and the swollen (i.e. saturated) state of the particles. The CF was made by mixing 10 g OPC and 100 g demineralized water for three hours with a mechanical stirrer, followed by filtration to remove the cement particles. To this end, 0.10 g polymer was mixed with 100 mL demineralized water or cement filtrate (CF, pH 12.6) [22]. After 24 h, a filter was used to collect the remaining water which was not absorbed. 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. (2):

$$\text{swelling capacity} = (m_0 - m_{\text{filtered}}) / m_{\text{SAP}} \quad (2)$$

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 initial dried SAP (i.e. 0.10 g). The filtration paper was typically saturated prior to filtration to exclude its

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