Benefits of pH-responsive superabsorbent polymers to stimulate autogenous healing of concrete cracks

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Use of superabsorbent polymers (SAPs) in concrete can stimulate autogenous healing of cracks in concrete. The SAPs, being cross-linked polymer networks, can absorb and retain aqueous solutions up to several hundred times their own weight. By swelling extensively, these SAPs can expand and block the cracks in concrete (self-sealing). In addition, they can release the absorbed water to induce further hydration of yet unhydrated binder particles near the crack walls and stimulate calcium carbonate precipitation, resulting in a regain in water-tightness and strength (self-healing). However, if the SAPs swell strongly during mortar mixing, the created macropores will negatively influence concrete strength. To meet this problem, pH-responsive SAPs can offer benefits. When the SAPs contain amine moieties, these will become protonated at pH values below their pKa, leading to repelling charges and an increase in swelling. For application in self-healing concrete, an increase in swelling when the pH drops from 13 to below 8-10, is desirable. In this way, on the one hand swelling will be limited in the highly alkaline fresh concrete mix and only small pores will be created by the swollen SAPs. On the other hand, since rainwater entering cracks in concrete will have a near-neutral pH, the SAPs will swell more at this moment and provide self-sealing.

Several synthetic and semi-synthetic SAPs were developed for self-healing applications. First, SAPs containing N,N'-methylene bisacrylamide (MBA) as a synthetic cross-linker have been studied. MBA was combined with acrylic acid (AA), with copolymers of AA and acrylamide (AM), and with dimethylaminoethyl methacrylate (DMAEMA) (containing amine moieties). Secondly, polysaccharides were introduced, including alginate, to create semi-synthetic SAPs. Subsequently, a stronger, covalent network was targeted by modifying alginate with methacrylic anhydride to incorporate methacrylate moieties (algMOD). AlgMOD was subsequently combined with carboxylic (AA) and sulfonic acids (2-acrylamido-2-methylpropanesulfonic acid, AMPS). Additionally, the effect of varying the degree of modification (DS) of algMOD on the swelling capacity, mortar strength and self-

healing capacity was assessed. Finally, pH-responsive monomers (DMAEMA and dimethylaminopropyl methacrylamide, DMAPMA) containing amine moieties were combined with methacrylated polysaccharides (algMOD).

The swelling capacity of the SAPs has been identified in aqueous solutions of varying pH and in cement filtrate solutions. For the SAPs containing acid moieties, the synthetic SAPs with AA and AM have strong swelling capacities going up to 456 g_{water}/g_{SAP} at pH 12. For the semi-synthetic SAPs, those composed of algMOD with a low DS combined with AA and copolymerized with AA and AM led to extremely strong swelling capacities (up to 630 g_{water}/g_{SAP} at pH 12). AlgMOD combined with AMPS led overall to the strongest swelling at neutral pH (195 g_{water}/g_{SAP}). The SAPs containing amine moieties generally have a lower swelling capacity. The SAP based on DMAEMA with a low amount of cross-linker led to 68 g_{water}/g_{SAP} at pH 3. ATR-IR spectroscopy indicated that most SAPs showed hydrolysis in aqueous solutions at extremely alkaline conditions (pH ≥ 12). The latter was observed less strongly in cement filtrate.

After characterization, the SAPs were incorporated in a standard mortar mixture to explore the bending and compressive strength of mortar after incorporation of 0.5 and 1 m% SAP with respect to binder weight. Additional water was added to create mixtures exhibiting a similar workability as the reference with a water-to-cement ratio of 0.50. Alginate-based SAPs (with AA) led to the smallest decrease in compressive strength, with the best results for algMOD with a high DS combined with AA (up to 7% decrease for addition of 1 m% SAP).

Finally, for the best performing SAPs, the degree of self-sealing and self-healing has been investigated by a water permeability test and a four-point-bending test on mortar samples. The introduction of 1 m% synthetic SAPs with AA and AM induced a strong self-sealing, with water permeability values close to the values of uncracked samples.

The four-point-bending test showed strong healing capacities of mortar with alginate combined with AA (strength regain up to 63% for cracks up to 65 µm, compared to 40% for the reference).

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