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SUPERABSORBENT BIOPOLYMERS FOR MITIGATING AUTOGENOUS SHRINKAGE IN CEMENT-BASED MATERIALS

A.N. Aday, W.V. Srubar III*
University of Colorado Boulder, ECOT 441 UCB 428, Boulder, Colorado, USA
*Corresponding author; e-mail: wsrubar@colorado.edu

Abstract
Availability of water plays an essential role in the hydration of ordinary portland cement. At low water-to-cement (w/c) ratios, for example, hydration processes can rapidly deplete water. The increased demand for more water exacerbates surface tension-induced stresses within fine capillary pores, which causes shrinkage of the cement paste. This phenomenon, termed autogenous shrinkage, is often prevented with sufficient curing, namely by keeping the surface of the concrete continuously wet. However, such conventional curing methods are not sufficient for ultra-high-performance concretes, which are produced with very low w/c ratios. In these applications, autogenous shrinkage is mitigated *via* the use of internal curing approaches, either by inclusion of prewetted lightweight aggregates or superabsorbent polymers (SAPs). SAPs are ultra-hydrophilic polymer networks capable of absorbing 100,000% of their dry weight in water. A variety of acrylic-based monomers are typically employed in the preparation of SAPs, as are a number of aggressive solvents and time- and energy-intensive polymerizations. This paper presents recent experimental efforts on synthesizing and characterizing superabsorbent polymers from biorenewable resources and principles of green chemistry. In this work, the chemical synthesis and physical swelling of superabsorbent biopolymers are investigated in (a) water and (b) synthetic concrete pore solutions. Results demonstrate that biobased SAPs that absorb in excess of 20,000% their weight in water can be synthesized using ambient-condition polymerizations and green solvents, thus offering a potential biobased solution to successfully mitigating autogenous shrinkage in ordinary portland cement paste and mortars.

Keywords:
Superabsorbent polymers; biopolymers; cement; concrete; internal curing.

1 INTRODUCTION

High performance concrete (HPC) is known for its enhanced durability and compressive strength and can be defined as having low water-to-cement (w/c) ratios between 0.20 and 0.35 [Jensen 2001]. Upon hydration of the OPC the process of self-desiccation occurs, in which menisci develop in capillary pores. These tension-induced stresses cause the hydrated cement paste to shrink. To prevent autogenous shrinkage an external supply of water must be applied to the HPC that provides moisture to the capillary pores, because the availability of bleed water is insufficient to prevent severe autogenous shrinkage [Aitcin 2013].

Previous research has shown that autogenous shrinkage can be mitigated with the use of internal curing agents, like prewetted lightweight aggregates [Jensen 2001] [Aitcin 2013] or superabsorbent polymers (SAPs) [Jensen 2002] [RILEM 2012] [Hasholt 2012]. In recent years, the use of SAPs as internal curing agents has been investigated and continues to be an active field of study [Hasholt 2012]. SAPs reduce autogenous shrinkage in HPC by serving as internal reservoirs of water, which is released during curing to reduce or eliminate self-desiccation by increasing the degree of cement hydration [Hasholt 2012] [Jensen 2001] [Jensen 2002]. Hygroscopic gels, such as SAPs (and the biobased SAPs investigated herein), provide water to the hydrating cement paste during the accelerated hydration period, with water that has desorbed from the gel matrix when the degree of hydration is approximately 0.6 [Friedemann 2009].

1.1 Superabsorbent Polymers

Superabsorbent polymers (SAPs) are crosslinked networks of ultra-hydrophilic polymers that can absorb 100,000% of their dry weight [Zohuriaan-Mehr 2008]. These polymer networks have ionic functional groups that aid in the ability to absorb fluids through ion-dipole interactions but also participate in coulombic repulsive interactions that makes the polymer chains rigid [Buchholz 1998]. The rigid nature of the crosslinks in the SAP network renders the polymer insoluble. Covalently crosslinked SAPs are generally formed when the monomer (acrylic acid) is copolymerized with a multivalent vinyl crosslinking agent (N, N'-methylene bisacrylamide) in a free radical polymerization. Previous research has demonstrated that the crosslinking agents modify the swelling behavior [Buchholz 1998]. A large share of polymerizations occurs in organic solvents due to the insolubility of monomer or crosslinking agent. Water is an excellent solvent for this polymerization primarily because the monomers, initiator, and crosslinking agent are all soluble in the aqueous solution [Buchholz 1998]. While petroleum-based SAPs are commonplace, there is much promise for using hydrophilic biopolymers, such as alginates, celluloses, and carrageenans [Feng 2014], for a new class of biobased SAPs.

1.2 Carrageenan

Carrageenans are a class of linear, hydrophilic polysaccharides that are present in various species of red seaweeds. The hydrophilic and anionic properties of carrageenans are employed for many commercial uses in foods and cosmetics as a thickening agent.

Defined by their chemical structure, carrageenans are strong anionic polymers, due to the presence of half-ester sulfate groups. Carrageenans are categorized according to the location and number of these sulfate groups and their corresponding functionality [Volery 2004]. Kappa-carrageenan (κC), for example, has one sulfate group on the C4 position of the 1,3-linked disaccharide units [Stanely 1987]. κCs are gelling types, whereas lambda carrageenans are not. This is due to the C4 conformation of κC, which is not present in lambda carrageenan [Campo 2009], allowing for helical structures that are central to gel formation.

1.3 Biobased SAPs

Biobased SAPs with carrageenan backbones have many desirable characteristics that provide useful advantages over purely petroleum-based SAPs. κCs have natural thermo-reversible gelling properties, they form gels in the presence of cations (K^+ and Ca^{2+}) [Campo 2009], and they have been shown to provide moisture-retaining properties that have been used in many non-food applications [Buchholz 1998] [Campo 2009]. Because κC is from red seaweeds, it offers the advantage of being a renewable and sustainable resource for biopolymeric monomers. In addition to petroleum-based precursors, another concern of SAP synthesis is the traditional solvents used, which, depending on the monomer, can be aggressive and hazardous. κC was chosen specifically because of its intrinsic hydrophilicity and solubility in water.

1.4 Research Objectives

To address the limitations of conventional SAP production, the objective of this work was to synthesize and characterize a superabsorbent biopolymer using green chemistry practices and ambient-condition free radical polymerization techniques. More specifically, a superabsorbent biopolymer was synthesized using κC and acrylic acid monomers and a thermal initiator that degraded at low temperatures. A "one-pot-reaction" solution polymerization technique was employed where no reaction vessels needed to be destroyed to remove the polymer. Once synthesized, the swelling behavior of the biobased SAPs were characterized in water and synthetic concrete pore solutions to assess their potential to mitigate autogenous shrinkage in cement-based materials.

2 MATERIALS AND METHODS

2.1 Materials

The polysaccharide backbone, κC, N, N'-methylene bisacrylamide (MBA), acrylic acid (AA), and ammonium persulfate (APS) were obtained from Sigma-Aldrich.

2.2 Synthesis of biopolymer

Deionized water (50mL) was first added to a beaker and heated to 70 ± 5°C in an oil bath. κC was added gradually and constantly stirred with a stir bar at 300 rpm until a homogeneous solution was achieved. Upon dissolution of the κC, AA was added followed immediately by MBA with continuous stirring for 5 min. After the elapsed time the water-soluble initiator, APS, was added to the solution and stirred until the viscosity increased to the point of gel formation. The gel was then hand-stirred for an additional 2 min. A 1M solution of sodium hydroxide (NaOH) was added to the gel for neutralization of carboxylic acid groups and hand stirred until the gel had absorbed the solution. The gel was then added to 100 ml of methanol to dewater for 1 hour. The methanol was decanted and fresh methanol was added to the gel to dewater for 24 hours. After removal from methanol, the gel was cast into plastic petri dishes and allowed to dry at ambient conditions (16% ±5% RH, 22.2°C ±2°C) for 7 days. Dried gel was ground into a powder, sieved to a 125-250 µm particle size, and stored away from heat, light, and moisture.

To minimize variables in the synthesis, only the amount of AA monomer was varied in order to investigate the swelling behavior at various AA concentrations. See Table 1 for a list of sample formulations.

Table 1. Biobased SAP sample formulations.

Sample	κC [g]	AA [mL]
S1	1.00	3.5
S2	1.00	2.5
S3	1.00	3.0

2.3 Solution Absorbency

Each dried sample was weighed and added to a 150 µm mesh bag then immersed in 50-100 ml of solution (deionized water, tap water, or a synthetic concrete pore ionic solution) at room temperature and allowed to swell in predetermined time intervals. The same methodology for water absorbency was employed for all solutions. Table 1 shows the ES measurements for all samples swollen in water and the pore solution. Equilibrium swelling (Q) was measured by removing the bag from the water and excess water was allowed to drain from the bag. After correcting for water absorbed by the bag, Q was calculated according to:

$$Q\left(\frac{g}{g}\right) = \frac{w_{wet} - w_{dry}}{w_{dry}} \quad (1)$$

where w_{wet} and w_{dry} are the weights of the moistened polymer and dry polymer, respectively.

A synthetic pore solution was synthesized to mimic the solution chemistry that is typically observed in ordinary portland cement hydration reactions [Ghods 2009]. This pore solution was chosen specifically to represent the median ion concentration in a concrete pore solution. The pH of the synthetic pore solution was 13.8. See Table 2 for pore solution chemistry.

Table 2. Synthetic pore (ionic) solution (g/mL).

$Ca(OH)_2$	K(OH)	Na(OH)	$Ca(SO)_4 + 2H_2O$

Sat.	11.22	4.00	13.77

2.4 Characterization of gel morphology

Scanning electron microscopy (SEM, JEOL JSM-6840LV) was performed using an accelerating voltage of 15 kV to analyze the polymer morphology. Non-powdered and powdered samples were attached to aluminum stubs using carbon tape and then sputter-coated with Au (Cressington 108auto) for 20-25 s at mA (~3.5 to 4.0 nm) in an Ar-rich environment.

3 RESULTS

Fig. 1 shows an SEM image of dried SAP (Sample S2). As expected, the particles exhibited an irregular shape attributed to manual grinding similar to SAPs previously synthesized by others [Krafcik 2016].

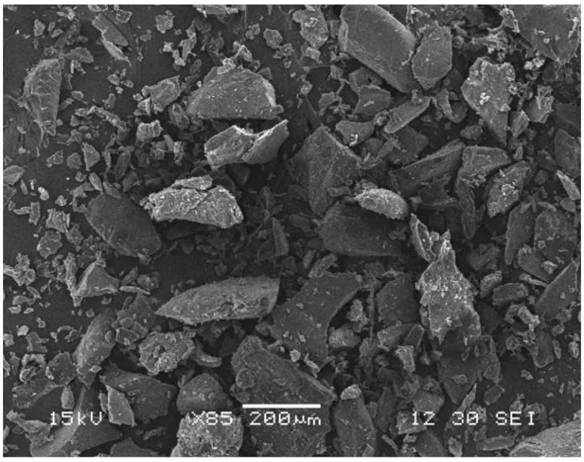

Fig. 1. SEM micrograph of dried SAP Sample showing particle sizes of 250 µm or less.

3.1 Water and Pore Solution Absorbency

Fig. 2 shows the swelling ratios of the polymer samples in deionized water in the first 120 minutes of swelling. All of the SAPs show a large initial increase in water absorption. Similarly, Fig. 3 shows the ES ratios for S1, S2, and S3 for 120 min of swelling. These samples also show large increases in pore solution absorbency in the first 1 min of swelling.

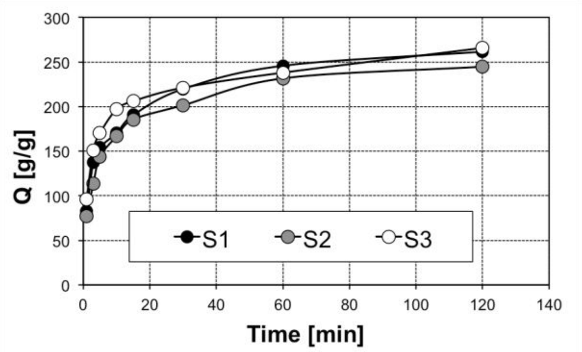

Fig. 2. Equilibrium swelling ratio (Q) of SAP samples in deionized water.

A summary of the equilibrium swelling ratio (Q) for the synthesized SAPs in tap and deionized water, along with the pore solution, are shown in Table 3. The values shown are the average of the highest swelling values obtained from three water absorbency trials. The Q ratio is defined as a 15% or less increase in Q between two time intervals. The samples swollen in tap and deionized water achieved equilibrium after 120 minutes, whereas S1, S2, and S3 samples swollen in pore solution achieved equilibrium after 15 min, 10 min, and 30 min, respectively.

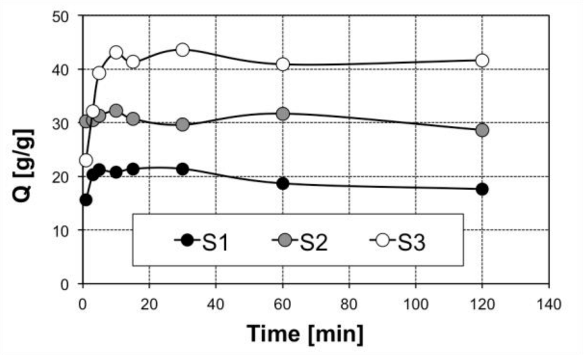

Fig. 3. Equilibrium swelling ratio (Q) of SAP samples in synthetic concrete pore solution.

Table 3. Maximum swelling of biobased SAPs.

Sample	DI Water	Tap Water	Pore Solution
S1	26,149%	23,003%	2,140%
S2	24,467%	21,334%	3,220%
S3	26,570%	21,442%	4,360%

In comparison to SAPs synthesized under similar reaction conditions, the Q of samples S1, S2, and S3 are comparatively larger, as shown in Figure 4. As previously reported, the ES ratio of a SAP sample of similar composition was 170.5 [g/g] [Pourjavadi 2004] compared to sample S1 with a swelling ratio of 261.5 [g/g] in deionized water.

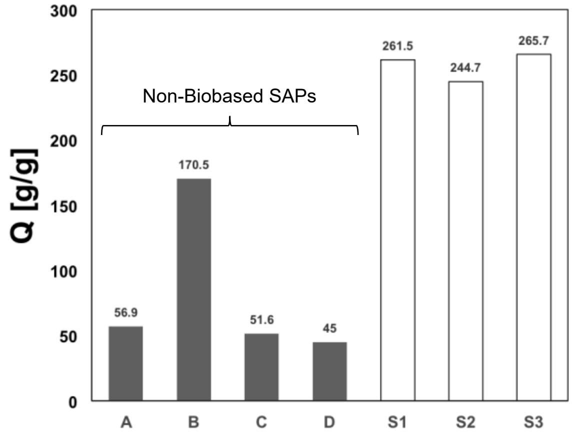

Figure 4. Summary of the performance of bio-based SAPs in comparison to non-bio-based SAPs [Pourjavadi 2004].

4 DISCUSSION AND FUTURE WORK

From these data the concentration of acrylic acid (AA) does not appear to influence absorption, indicating that, even at lower AA concentrations, the polymer will absorb large amounts of water. These findings suggest that the natural swelling ability of the Kappa-carrageenan (κC), due to its intrinsic hydrophilicity, could be largely responsible for the swelling capacity of the synthesized biobased SAPs. This is an advantage to having a biobased SAP, where even with minimal AA concentrations, the κC will allow for absorption (and presumably desorption) of fluids.

It is evident from Fig. 2 and Fig. 3, that the ion concentration has an effect on the swelling kinetics of all SAP samples. Even with exposure to cations, the ability for the SAP to swell in solution is evident.

However, the fluctuation in swelling behavior in the pore solution for all samples indicates the competition between cations and the polymer's affinity to uptake water, which provides clues to the swelling kinetics of the SAP in highly alkaline environments. While the absorption of the pore solution is decreased compared to the aqueous solutions, the SAPs still absorb over 1000% of their original weight. This can be attributed to the ability of κC to form gels, even in the presence of K^+ and Ca^{2+} ions [Therkelsen 1993] [Campo 2009].

The presentation of the swelling properties of these biobased SAPs suggest that these materials are good candidates for internal curing agents in low w/c cement and concrete mixes. Non-biobased SAPs with similar swelling ratios have been used to effectively mitigate autogenous shrinkage in cement mortars and concretes [Krafcik 2016] suggesting that these SAPs would exhibit similar performance. As an internal curing agent, SAPs, such as those investigated herein, provide an advantage in that they can be specifically tailored to mitigate autogenous shrinkage in HPC by controlling the water absorption and the shape and size of the SAP particles [RILEM 2012].

The shape and size of the particles will be investigated in future work to determine its effects on the swelling behavior in aqueous and synthetic pore solutions. It has been shown that the particle size of the SAP does affect the rate of absorption and the maximum absorption capacity [Esteves 2011]. Measures should be taken to investigate the mechanical alteration of the shape of the dry polymer to represent more spherical shapes. The swelling behavior of these shapes may align better with the capillary pore structure and allow for increased hydration of the cement paste and mortar mixes. By decreasing the size of the SAPs, it may prove difficult to fully investigate the swelling behavior as the swelling capacity has been shown to increase non-linearly as the diameter of the SAP particle is increased [Esteves 2011].

5 SUMMARY

In this work, superabsorbent biopolymers derived from kappa-carrageenan (κC) were synthesized and their swelling behavior was characterized in tap water, deionized water, and synthetic concrete pore solution. The effect of acrylic acid monomer content on the swelling behavior was explicitly investigated, as was the time to equilibrium swelling. Results show that the ranges of equilibrium swelling (~2-27,000%) achieved by the biobased superabsorbent polymers (SAPs) investigated herein were on par with other previously produced non-biobased synthetic SAPs, even with minimal acrylic acid content. The promising evidence suggests that the biobased SAPs would aid in mitigating autogenous shrinkage in cement paste, mortars, and concrete. However, incorporation of the synthesized biobased SAPs into cementitious binder systems is in need of further investigation.

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