

# Thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel particles improve workability loss and autogenous shrinkage in cement paste

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## ABSTRACT

In this work, we show that non-superabsorbent, thermo-responsive poly(*N*-isopropyl acrylamide) (PNIPAM) hydrogel particles (< 250 μm) can reduce autogenous shrinkage in cement paste and improve early-age stiffening that can be caused by traditional superabsorbent polymers (SAPs). Swelling measurements in DI water and cement filtrate solution suggest that SAP-induced early-age stiffening is caused by its super-absorbency in low-ionic solutions – a behavior not exhibited by non-superabsorbent PNIPAM. Addition of PNIPAM resulted in a 29% and 60% reduction in autogenous shrinkage strain at 14 days when used alone (0.3 wt% PNIPAM) and in combination with SAP (0.15% PNIPAM, 0.15% SAP), respectively, compared to a Control with no polymer addition. Furthermore, an addition of 0.3 wt.% PNIPAM exhibited a ~29% and ~37% decrease in static yield stress compared to a Control and 0.3 wt% SAP-modified cement pastes, respectively. Taken together, the results provide initial evidence to suggest that the use of hydrogels as internal curing agents may not necessarily require super-absorbency to reduce autogenous shrinkage. Non-superabsorbent hydrogels, like PNIPAM, may help reduce autogenous shrinkage while alleviating the effects of SAP-induced early-age stiffening.

## 1. Introduction

Rapid urbanization around the world is causing a demand for high and ultra-high-performance concrete (UHPC). The UHPC market is expected to reach USD 642 million by the year 2027 [1]. UHPC is a class of cementitious materials known for its excellence in durability, reduced penetrability to ions (*i.e.*, chlorides and sulfates) and carbon dioxide, and high early-age compressive strength [2,3]. However, the low water-to-cement ratio (*w/c*) and the use of silica fume can lead to chemical, autogenous, and drying shrinkage, which can promote cracking [3,4].

To mitigate shrinkage in UHPC systems, internal curing *via* superabsorbent polymers, or SAPs, are have been utilized as a novel internal curing agent [5,6]. SAPs are hydrophilic, chemically crosslinked polyelectrolytes with an ability to swell more than 1000 times their dry weight. While SAPs have been used successfully for mitigating autogenous shrinkage (AS) [7] and self-healing [8], SAPs can generate workability issues due to their superabsorbent properties [9]. Additional

mixing water or superplasticizers must be added to overcome the workability loss that is typical of SAP-modified cement paste and concrete. SAP absorption and related kinetic processes can vary considerably depending on the chemical composition of the SAP, the particle shape and size, as well as the composition of the absorbed fluid [10,11]. Therefore, the determination of accurate absorption capacities and subsequent desorption of SAPs with pre-testing through swelling experiments is an essential first step. Over- or underestimations of absorption capacity can impart unintended changes to the microstructure of cement paste in the fresh- and hardened-state, thereby influencing the rheology and internal curing performance.

We hypothesized that, while SAPs have been highly regarded for their “super” absorption capacities, other smart hydrogels that respond to environmental stimuli (*e.g.*, water, temperature, pH), such as acrylamide-based hydrogels, could provide some water-control and internal curing similar to SAPs without the consequences related to their super-absorbency and sensitivity to complex ionic cement pore fluids.

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### 1.1. Workability loss in SAP-modified cement paste

Due to the chemical nature of most SAPs, namely, that they are primarily composed of acrylate-based polymers (*i.e.*, poly(acrylic acid)), they are not chemically inert [12]. It has been shown in numerous studies that the adsorption and desorption behavior of SAPs is heavily influenced by multivalent cations (*i.e.*,  $\text{Ca}^{2+}$ ) in solution, such as those present in synthetic cement pore solutions and freshly mixed cement paste, mortar, and concrete [13–15]. At early ages in fresh-state cement paste, the ion concentration with respect to  $\text{Ca}^{2+}$  can vary between 0.23 mM and 25.9 mM (depending on the  $w/c$ ), but the monovalent cations can be higher [16]. Within the first few minutes of exposure to the mix water and prior to complexation with abundant free  $\text{Ca}^{2+}$ , SAPs have a high affinity to absorb large amounts of water in minutes due a Donnan membrane effect, which occurs when a charged porous medium (*i.e.*, SAPs) are in contact with an ionic solution [17,18]. To maintain electroneutrality, the concentration of counterions in the SAP will increase, leading to a chemical potential gradient with the surrounding water, thus causing the SAPs to swell until the net osmotic pressure is zero [19–21]. The reduction in the available water due to the sorption of the SAPs at early ages can cause a decrease in the workability of fresh-state cement paste. In highly multivalent cationic solutions typical in later ages of mixing, SAPs can deswell and release their stored water due to the complexation of the carboxylic acid groups present in the polymer network with available  $\text{Ca}^{2+}$  ions in solution. This complexation causes a collapse in the polymer network and the consequent deswelling of water. The severity of this change in rheological behavior is dependent on factors such as  $w/c$  ratio, the addition of supplementary cementitious materials (SCMs), and use of superplasticizers or additional mixing water—two strategies most often used to overcome the workability loss associated with the use of SAPs [5,13,21–24].

While there are limited studies reporting on the rheological influence of SAPs on cementitious materials, it has garnered more research interest with the emergence of self-consolidating lightweight concrete (SCLWC), 3D concrete printing technologies, and UHPC systems. As previously mentioned, the SAP absorption/desorption behavior can lead to dramatic changes in rheological properties, such as an increase in the yield stress and viscosity if no additional water or superplasticizer is added to compensate for the workability loss. Stiffening is a loss of workability, which is related to the increase in the static yield stress and plastic viscosity of SAP-modified cementitious systems. The stiffening is due to the intrinsic sorption properties of the SAPs and the ionic conditions of the surrounding fluids, which affects the workability of the mixtures. While the stiffening of cementitious materials (*i.e.*, the increase in static yield stress and plastic viscosity) could be considered a negative effect, an increase in the static yield stress and viscosity is beneficial for shotcrete, SCLWC, and 3D concrete printing applications [22,25,26].

### 1.2. Autogenous shrinkage of SAP-modified cement paste

Self-desiccation in UHPC systems leads to autogenous shrinkage and increased cracking potential [27]. Higher-than-normal cement contents, resulting in low  $w/c$  ratios ( $w/c < 0.35$ ), and utilization of SCMs, like silica fume, in UHPC result in a denser microstructure and, as a result, increased autogenous shrinkage [28]. Water content and pore size of the cement paste influence autogenous shrinkage, so it is not surprising that autogenous shrinkage is a concern when designing UHPC. Less than 24 h after mixing when cementitious materials have not gained maximum strength, internal stresses induced by self-desiccation can exceed the strength of the cementitious matrix, leading to crack formation. At these early stages, crack development is on the order of  $<10 \mu\text{m}$  (micro-cracks), whereas at later ages, these cracks can become wider ( $>10 \mu\text{m}$ ), thus impairing the strength and durability of the concrete structure. To this end, methods for mitigating or fully preventing autogenous shrinkage in cementitious materials, especially in UHPC systems,

through the use of internal curing agents has become increasingly important.

Internal curing agents, namely lightweight aggregate (LWA), clays, or SAPs [7,29,30], have been employed to mitigate autogenous shrinkage. The general mechanism of internal curing by SAPs is based on the release of stored water from a crosslinked polymer network, typically obtained from the mixing water, and delivered to the cementitious matrix during the hydration process. In this way, the addition of SAPs have been shown to reduce and even completely mitigate autogenous shrinkage. Careful consideration of the size and dosage of SAPs to mitigate autogenous shrinkage is a critical initial step in the mixture design aspect, where literature values report the average particle size is typically  $<600 \mu\text{m}$  and dosages range between 0.1 and 0.7 wt% (by weight of cement) [5,11,14,31].

While fluid absorption and release from SAPs is a key feature when SAPs are used as internal curing agents, contrary results have been reported on the rate of water release and the ability of SAPs to mitigate autogenous shrinkage [32,33]. Schrofl et al. showed that highly anionic SAPs cause a fast release of absorbed fluid and, thus, did not provide autogenous shrinkage mitigation [15]. However, recent work by Zhong et al. found that zwitterionic SAPs (*e.g.*, SAPs that have cationic and anionic character) exhibited excellent internal curing performance [7] even though they displayed a rapid liquid release. In earlier work by Krafcik and Erk, SAPs with relatively fast water release were also found to provide reductions in autogenous shrinkage [13].

Considering that there is no consensus on whether slow versus rapid water release is preferred or required for SAP to mitigate autogenous shrinkage, we looked to a new class of non-superabsorbent phase change materials that are instead designed to be slow and thermo-responsive in their water release properties to assess their efficacy at reducing SAP-induced workability loss and autogenous shrinkage. Polyacrylamides have previously been incorporated into acrylate-based SAPs and have exhibited stable swelling behavior in high ionic solutions, as well as greater void-filling ability and microstructural refinement of the cement paste [34,35]. Due to the thermo-responsiveness of some polyacrylamides and the temperature changes that occur within cementitious materials, a thermo-responsive polyacrylamide-based hydrogel, namely poly(*N*-isopropylacrylamide) (PNIPAM), was identified as an alternative polymer chemistry to SAPs to provide modified workability and differing water-release kinetics that can be associated with the chemical composition of SAPs (*i.e.*, poly(acrylic acid)).

### 1.3. Scope of work

In this work, we investigated the effects of adding non-superabsorbent, thermo-responsive hydrogel particles on rheological properties and autogenous shrinkage in low  $w/c$  ratio cement paste. PNIPAM is a non-superabsorbent, thermo-responsive hydrogel well studied for its volume phase change behavior upon heating in aqueous solutions [36–38], where its inverse solubility properties at elevated temperatures are contrary to the behavior of most polymers [39]. PNIPAM hydrogels reversibly undergo a phase change from a hydrated (swollen) gel to a dehydrated (collapsed) gel in response to increases in temperature in aqueous solutions [38]. The amide groups of PNIPAM promote hydrophilic interactions, while the isopropyl side chains are hydrophobic [40]. The transition from a hydrophilic to hydrophobic material occurs at the lower critical solution temperature (LCST), experimentally determined to be  $\sim 32^\circ\text{C}$  [41]. PNIPAM has been synthesized into single chains [42], crosslinked gels [43], latexes [44], and nanotubes [45].

Herein, we assess the ability of a crosslinked hydrogel particle form of PNIPAM as a novel dry polymer admixture to reduce early-age stiffening caused by SAP-modified cement pastes and reduce autogenous shrinkage. The swelling properties of each polymer were first measured to determine swelling capacities prior to their application in cement paste. The swelling characteristics of each polymer were studied in both

deionized water and cement filtrate solution to mimic very early- and late-age mix water chemistry. Isothermal conduction calorimetry (ICC) was then used to investigate the effects of polymer admixtures on the kinetics of cement hydration. The effect of SAP and PNIPAM on the fresh-state properties of cement paste, namely changes in rheology and setting time, were investigated without the addition of SCMs or water-reducing superplasticizers to fully examine the effects of the hydrogels alone. Rheology experiments using stress growth tests were performed to quantify changes in the static yield stress of polymer-modified cement pastes. Finally, autogenous shrinkage was measured in pastes containing SAP and PNIPAM to evaluate the potential for reducing early-age shrinkage due to self-desiccation.

## 2. Materials and methods

### 2.1. Materials

The cement used in this study was commercially available Type I/II OPC, which complied with ASTM C150 (Quikrete™). The chemical composition of OPC obtained via X-ray fluorescence (XRF Bruker S8 Tiger) is shown in Table 1.

Biobased SAPs were synthesized in-house according to the method reported in [14]. Biobased SAPs utilized in this study are a crosslinked copolymer of  $\kappa$ -carrageenan and poly(acrylic acid). PNIPAM was also synthesized in-house via the method reported in [46]. The PNIPAM is a crosslinked homopolymer of N-isopropylacrylamide and was chosen for this study based on its structural stability under repeated phase transitions in water, as reported in [46].

#### 2.1.1. Mixture proportions

Cement pastes with a  $w/c = 0.35$  were prepared for all tests. For samples containing SAP and/or PNIPAM, the dry polymer was hand-mixed into the cement until a uniform dry mixture was observed. Water was then added to the dry mixture and hand-mixed for 2 min in a mixing bowl until a homogenous mixture was achieved. No additional mixing water was added to SAP- or PNIPAM-modified cement paste samples to examine the effects of polymer addition on the static yield stress and autogenous shrinkage. Additionally, no SCMs or superplasticizers were used in this study to improve the workability of cement pastes, as these materials would impact the results of the rheology testing and autogenous shrinkage measurements.

Table 2 shows the mixture proportions with additions of dry polymers. A reference sample (Control) was prepared as a neat cement paste for comparison. Dry polymer additions were maintained at a maximum of 0.3 wt% by weight of cement.

### 2.2. Experimental methods

#### 2.2.1. Polymer swelling characteristics

The swelling capacities of SAP and PNIPAM were determined by the teabag method [47] in deionized (DI) water and cement filtrate (CF) with a  $w/c = 10$ , as reported in previous literature [16]. CF was prepared by adding 100 g of Type I/II cement to 1 L of deionized water. The slurry was covered with parafilm and stirred at 400 rpm for 24 h before use. The solution was filtered (Whatman Quantitative filter paper, pore size 2.7  $\mu\text{m}$ ) prior to testing to remove large particulate. All dried polymer samples were mechanically ground and sieved to a 125–250  $\mu\text{m}$  particle size. For each solution, three trials for absorption and desorption were conducted.

The swelling ratio ( $Q$ ) was measured in time intervals of 1, 3, 5, 10,

**Table 1**

Chemical composition of Type I/II OPC.

Oxides (wt.%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	MgO	SO <sub>3</sub>	LOI
OPC	19.7	4.38	62.0	3.33	0.76	0.19	1.38	3.32	2.96

**Table 2**

Mixture proportions. Total polymer addition was held constant at 0.3 wt% by weight of cement for isothermal conduction calorimetry, time of set, and autogenous shrinkage tests. Samples containing 0.15 wt% SAP or 0.15 wt% PNIPAM were only used in rheology testing. The  $w/c$  ratios were held constant for all experiments.

	Water-to-Cement Ratio ( $w/c$ )	Polymer (wt.% of cement)	
		SAP	PNIPAM
Control	0.35	-	-
SAP	0.35	0.15	-
SAP	0.35	0.3	-
PNIPAM	0.35	-	0.15
PNIPAM	0.35	-	0.3
SAP+PNIPAM	0.35	0.15	0.15

15, 30, 60, and 120 min. After correcting for solution 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 masses of the moistened polymer and dry polymer, respectively.

#### 2.2.2. Isothermal conduction calorimetry

A TAM Air 8-channel Isothermal Conduction Calorimeter (ICC) (TA Instruments, New Castle, DE, USA) was used to measure the rate of heat evolution and the cumulative heat of hydration of fresh cement pastes without and with polymers. The ICC bath temperature was set to 20 °C and allowed to reach equilibrium over a 24 h period. To minimize noise, an initial and final baseline measurement was taken for 1 h. Samples were hand-mixed for 2 min in a mixing bowl. Then, ~ 15 g of cement paste was added to the glass ampoules, massed, and placed in the calorimetry block. Heat flow data were collected for 72 h for all mixtures. All data were normalized with respect to the total mass of cement, water, and polymer (mW/g).

#### 2.2.3. Rheology

An MCR 301 rotational rheometer (Anton Paar, Graz, Austria) was used to determine the effect of SAP and PNIPAM addition on the rheological properties of fresh pastes at various early ages of 5, 10, 15, and 30 min after mixing. Specifically, static yield stress was determined for each sample from stress growth testing. A 25-mm diameter stainless steel parallel plate geometry was used for all measurements. The top plate was cross-hatched to minimize the influence of slip. The gap between the plates was set to 1 mm and the temperature was kept constant at 20  $\pm$  0.1 °C. Cement pastes containing hydrogels were hand mixed to achieve a homogenized powder prior to water addition. Each mixture was hand-mixed for 2 min, in line with previous mixing procedures utilized in this study. Prior to each stress growth test, approximately 1 mL of fresh cement paste was loaded into the rheometer, and a cover was used during testing to prevent drying of the sample. The sample was allowed to rest in the rheometer before initiating the first test cycle, starting at 5 min.

The stress growth test consisted of a linear increase in the shear rate from 0.01 to 0.30  $\text{s}^{-1}$  over a 90 s test period, starting at 5 min after the cement had contact with water. The sample was then allowed to rest in between test measurements of 10, 15, and 30 min. Due to the inconsistent and irregular behavior of the cement paste, the results of the first cycle (5 min) were neglected and considered as the pre-shear protocol in

order to eliminate any previous shear history. This observation of irregular rheological behavior of SAP modified cement paste was also reported by Agostinho et al. [48]. Due to the dependency of static yield stress on the cement paste shear history, static yield stress testing was conducted on the same sample from the same mixture. All tests were terminated at 30 min to neglect the effects of cement hydration. Static yield stress measurements were performed in triplicate for each specimen.

#### 2.2.4. Time of initial and final set

Time of set was conducted according to [49]. Specimens were cured for 30 min in a moist chamber ( $90\% \pm 3\%$  RH,  $18 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ ). Measurements commenced after the curing period and were recorded every 15 min until the final set, which was defined as the time at which no circular impression was left by the needle on the paste sample. Table 3 summarizes the initial and final setting times of cement paste samples. From these data, it is evident that, unlike SAP, PNIPAM does not cause an increase in initial and final set times. Furthermore, the addition of PNIPAM and SAP in combination also resulted in initial and final set times akin to the experimental Control. These data were used to set the test parameters for autogenous shrinkage.

#### 2.2.5. Autogenous shrinkage

Autogenous shrinkage samples were prepared and measured according to previously published literature [14]. Measurements commenced at the time of final set (Day 0) and were recorded for 14 days ( $18 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ ,  $50\% \pm 2\%$ ). Four samples of cement paste, including a reference (Control) and three with dry polymers (SAP, PNIPAM, and SAP+PNIPAM) with a  $w/c = 0.35$  were prepared without superplasticizer (see Table 2 for sample compositions). These data were used to examine the efficacy of SAP and PNIPAM alone and in combination on mitigating autogenous shrinkage of cement paste.

### 3. Results and discussion

#### 3.1. Polymer swelling characteristics

The pH- and temperature-dependent swelling characteristics of SAP and PNIPAM in both DI water and cement filtrate (CF) solution are shown in Fig. 1 (pH dependence) and Fig. 2 (temperature dependence). Fig. 1 shows the isothermal pH-dependent swelling behavior of SAP and PNIPAM in deionized water (DI water) (pH 7) and CF (pH 13) solutions. Expectedly, the overall equilibrium swelling ratio ( $Q$ ) of SAP is dependent on the pH of the solution, as previously reported in [50]. For example, in pH 7 DI water, SAP exhibited a  $Q = 270 \pm 39 \text{ g/g}$  at 120 min. In the CF solution (pH 13), SAP shows a reduction in swelling capacity at  $5.8 \pm 0.4 \text{ g/g}$ . Well reported in the literature, the decrease in swelling capacity of SAP in highly alkaline environments is attributable to the presence of mono and divalent cations (*i.e.*,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ), which ionically crosslink with the anionic groups of acrylate-based SAPs, effectively reducing the osmotic pressure driving force of SAP swelling [51–54]. Furthermore, swelling capacity of SAPs can vary greatly depending on the synthesis route (*i.e.*, commercially purchased, or in-house synthesis), the anionic functional groups on the polymer backbone, and the crosslinking density of the polymer [20,55, 56].

**Table 3**  
Initial and final setting time of cement pastes with polymer additions of 0.3 wt% of cement.

	Initial Set (min)	Final Set (min)
Control	186	288
SAP	257	400
PNIPAM	156	240
SAP+PNIPAM	172	235

This result illustrates the propensity of SAPs to absorb high amounts of mix water at very early ages, during which the complexation of the SAPs with  $\text{Ca}^{2+}$  cations have not yet come to an equilibrium. Thus, the SAPs have not yet experienced an increase in the ionic crosslinking and corresponding reduction in swelling capacity. The swelling capacity reduces by two orders of magnitude as the ionic concentration approaches that of cement filtrate. This superabsorbent behavior in low-multivalent-ionic solutions (*i.e.*, low  $\text{Ca}^{2+}$  concentrations) and non-superabsorbent behavior in high-multivalent-ionic solutions is the likely cause of early-age stiffening of SAP-modified cement paste and concrete.

In contrast, Fig. 1 substantiates that the ionic dependence of non-superabsorbent PNIPAM was less pronounced than SAP. In pH 7, the swelling capacity of PNIPAM was  $7 \pm 0.4 \text{ g/g}$ . At pH 13 in CF solution, the swelling capacity decreased to  $5.7 \pm 0.7 \text{ g/g}$ , a magnitude identical to SAP swelling under the same pH conditions. In other words, PNIPAM absorbs nearly identical amounts of water in low- and high-ionic solutions, thereby circumventing the transition from superabsorbent to non-superabsorbent characteristic of SAPs as mix water increases in ionic concentration. In addition, results indicate that PNIPAM and SAP absorb identical amounts when immersed in CF solution, thereby illustrating that both can provide the same amount of internal curing water as the pore solution reaches its maximum ionic concentration and the paste begins to harden.

Fig. 2 shows the temperature-dependent swelling behavior of SAP and PNIPAM in DI water (pH 7) and CF (pH 13) solutions. SAP and PNIPAM particles were pre-soaked in DI water for at least 2 h prior to deswelling in DI water and CF solution to examine water release properties as the temperature of the aqueous and ionic solutions increased to  $70 \text{ }^\circ\text{C}$ . From Fig. 2, it is evident that the deswelling behavior is temperature dependent, as the deswelling was identical in the DI water and the CF solution for PNIPAM.

The temperature-dependent swelling behavior of SAP in DI water was markedly different from its swelling behavior in CF solution. SAP in DI water experienced a slight increase in  $Q$  of 5% from  $20 \text{ }^\circ\text{C}$  to  $70 \text{ }^\circ\text{C}$ . This increase was expected, as SAPs exhibit a temperature-dependent diffusivity which increases its swelling rate at elevated temperatures [12]. In CF, however, SAP released 99% of its stored water around  $35 \text{ }^\circ\text{C}$ . Because SAPs were fully swollen with water prior to deswelling in CF (to simulate a SAP pre-soaking condition), it was anticipated that the chemical potential gradient of the CF solution would cause the deswelling of the SAP, since SAP absorption is driven by osmotic pressure [54]. It is evident that the complexation of dissolved cations in the CF with the anionic functional groups of the SAP drive the deswelling regardless of the temperature of the solution, as this effect on deswelling is not observed in DI water upon heating. These data illustrate that as the hydration of cement occurs and various cations are released into the pore solution (*i.e.*,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ), SAPs will begin to release stored water into the system.

Contrastingly, PNIPAM immediately began to release its stored water upon heating in both DI water and CF solution and continued to release stored water over the duration of the experiment. This behavior was expected, given the temperature-dependent behavior of PNIPAM around its reported LCST [46]. With an increase in temperature from  $20 \text{ }^\circ\text{C}$  to  $35 \text{ }^\circ\text{C}$  of the DI and CF solutions, PNIPAM exhibited a reduction in  $Q$  of 57% and 49%, respectively. At  $70 \text{ }^\circ\text{C}$ , PNIPAM released 94% of its stored water in both DI water and CF solution. Overall, the results show that the temperature of the solution is the dominating factor in the deswelling behavior of PNIPAM in both DI water and CF solution.

Previous studies showed that SAP absorption in actual cement paste is approximately half the amount of water absorbed in a synthetic pore solution (*i.e.*, solution, like CF) [32,57]. Therefore, the absorption and desorption behavior of SAPs shown here is a conservative (extreme) case. While the chemical composition of the CF solution is higher in ionic strength than that of an actual hydrating cement pore solution, SAP swelling and deswelling behavior would exhibit identical pH- and

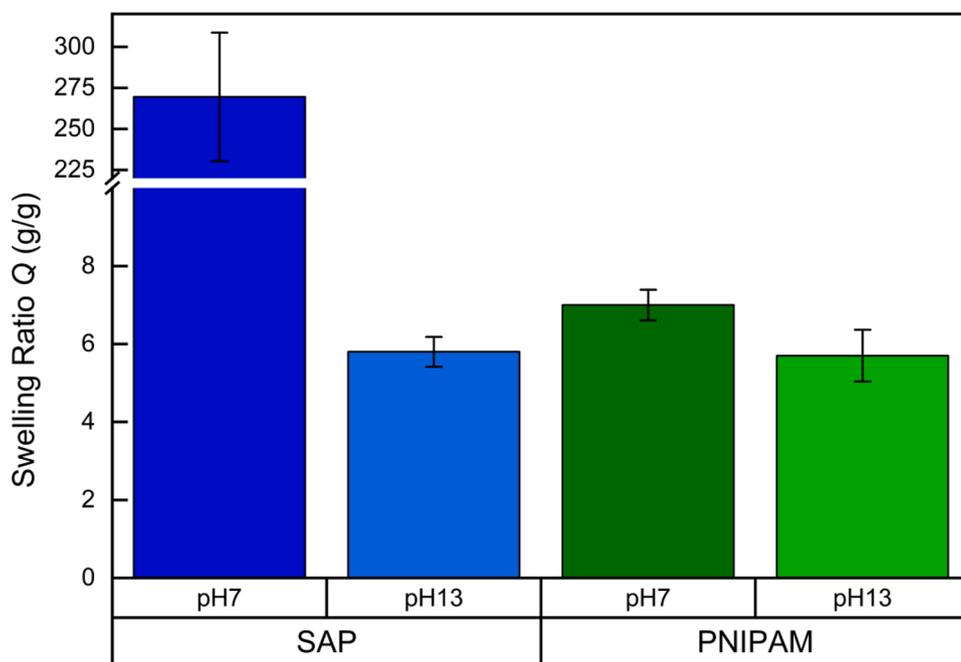


Fig. 1. Swelling ratio Q (g/g) of SAP and PNIPAM in DI water (pH 7) and CF (pH 13) at 120 min at ambient conditions ( $20 \pm 1$  °C).

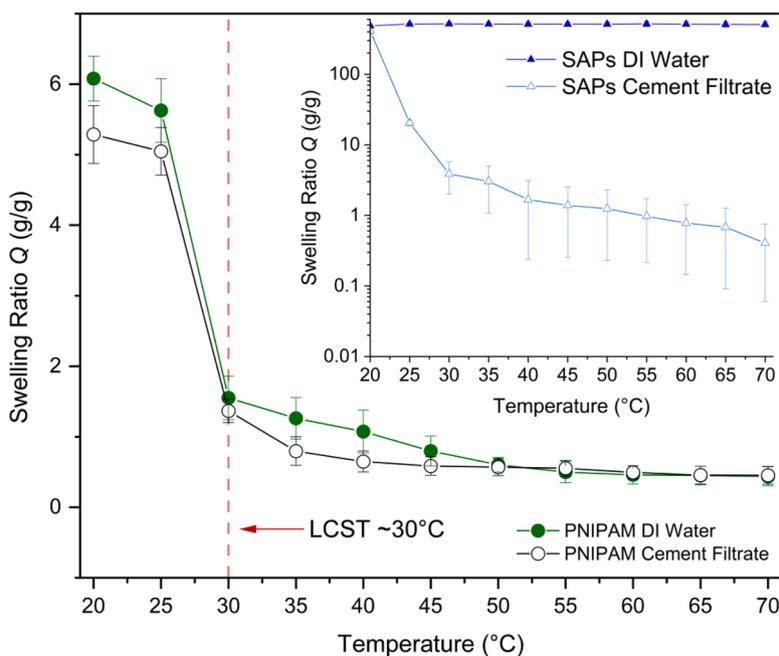


Fig. 2. Swelling ratio Q (g/g) of SAPs (inset) and PNIPAM as a function of temperature in DI water and CF solution. The LCST represents the hydrophilic-to-hydrophobic transition of PNIPAM.

temperature-dependent characteristics.

On the contrary, PNIPAM released approximately half of its stored water until the LCST was reached, above which the remaining portion of water was released as the temperature of the solution was increased regardless of the chemical environment. PNIPAM would behave identically in DI water (low ionic solution) and a late-age cement system (high ionic solution). Mechanistically speaking, a thermo-responsive polymer like PNIPAM with a tunable LCST ( $\sim 30$  °C) which is around the midpoint of the maximum internal temperature for curing cement (70 °C) is beneficial [58,59]. Reaching the LCST initiates a hydrophilic-to-hydrophobic transition, thereby triggering the continued release and repulsion of water regardless of the chemical environment,

as evidenced by data in Fig. 2. Thus, it is expected that water would be released from (and repelled by) PNIPAM once the internal curing temperature of the cementitious material reached the LCST regardless of the concentration of ions in solution, rendering the PNIPAM chemistry ideal for the controlled, temperature-dependent release of water in an actual hydrating portland cement paste.

### 3.2. Isothermal conduction calorimetry

Fig. 3 shows the heat flow and cumulative heat from isothermal conduction calorimetry (ICC) measurements of a reference 0.35 w/c cement paste (Control) and pastes containing SAP, PNIPAM, and

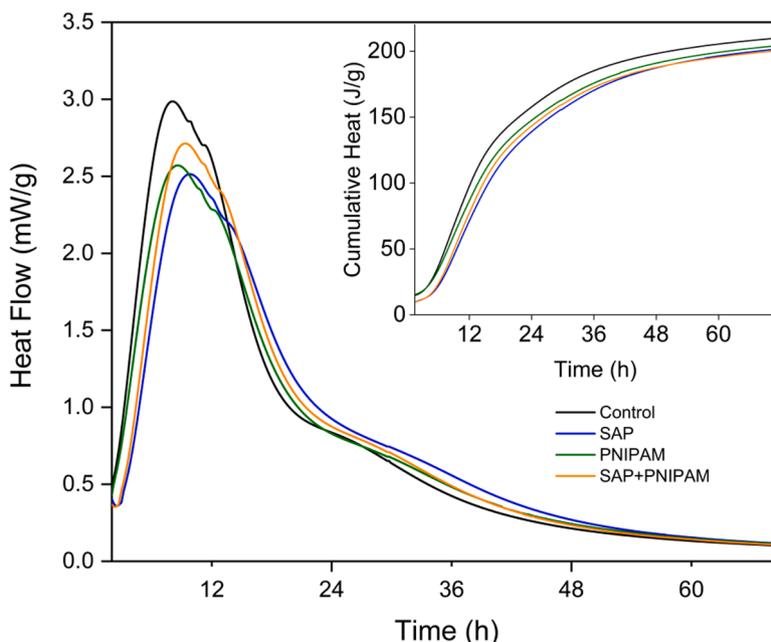


Fig. 3. Heat flow and cumulative heat (inset) curves for OPC Control paste without and with dry polymer addition of 0.3 wt%.

SAP+PNIPAM. Due to external mixing of the samples, the initial heat peak, corresponding to the addition of the mixing water and initial wetting/dissolution of cement particles, could not be measured. It was observed that the addition of SAP caused a delay in the onset of the acceleration period and a slight reduction in the overall heat flow in cement pastes, as expected given similar results published in other studies [19]. The main peak for SAP samples occurred approximately 9.8 h after mixing. In contrast, the main peak for the Control and PNIPAM-modified samples occurred near 8 and 8.8 h, respectively. We posit that, due to the increased alkali concentration in the Control and the PNIPAM samples (*i.e.*, PNIPAM does not complex with  $\text{Ca}^{2+}$ ), a higher pH in the cementitious pore fluid occurs and accelerated hydration is observed [60]. A reduction in the peak thermal power was observed for all polymer-modified samples. The shifting of the heat flow peaks and reduction in heat flow for polymer-modified samples could indicate an early release of water. An early release effectively increases the  $w/c$ , which corresponds to a decrease in the main hydration peak [61]. The addition of SAP+PNIPAM slightly increased the heat flow and decreased time to the main hydration peak, approximately 9.5 h. In essence, SAP-PNIPAM exhibited an averaged thermal behavior of both samples containing SAP or PNIPAM.

The inset plot of Fig. 3 shows cumulative heat gain (*i.e.*, heat of hydration). For these samples it was observed that the Control paste exhibited a higher cumulative heat, followed by pastes with PNIPAM, SAP+PNIPAM, and SAP. Similar observations were reported by Jansen et al. [62]. Plain cement pastes with higher  $w/c$  have higher cumulative heat gain because more water is available to allow the reaction to proceed [63]. The addition of SAP slightly decreased the cumulative heat of hydration in cement pastes at 0.3 wt%. It is evident that SAPs decrease the cumulative heat even at low additions of 0.15 wt%, owing to their complexation with  $\text{Ca}_2^+$  ions with acrylate groups present in the SAP and corresponding unavailability to produce cement hydration products. However, the incorporation of PNIPAM aids in a slight increase in cumulative heat, indicating an increase in the overall degree of hydration of cement pastes containing PNIPAM. This slight increase in the cumulative heat of hydration for PNIPAM cement pastes could be attributed to the fact that PNIPAM neither complexes with  $\text{Ca}^{2+}$  nor is it superabsorbent, therefore more  $\text{Ca}^{2+}$  and water are available for cement hydration. Additional data regarding maximum heat flow and corresponding 24- and 72-h cumulative heat can be found in the

Supplemental Materials (Table SM.1.).

### 3.3. Rheology

#### 3.3.1. Influence of polymers on fresh cement paste

Static yield stress measurements of cement paste are reported at 30 min after addition of water, without and with polymer additions, on cement paste samples (Fig. 4(a)). The static yield stress was determined at the peak value of the shear stress versus time plot (Fig. 4(b)), which corresponds to the static yield stress as described in [64,65].

The addition of SAPs caused an increase in the static yield stress at both dosages. An increase in dosage from 0.15 wt% to 0.3 wt% exhibited an increase in the mean static yield stress, but the data variability suggested that the increase was not necessarily statistically significant. In addition to high absorption of water, SAP particles can cause an even lower water content in the paste surrounding the SAP, which can induce micro-flocculation, thus causing additional increases in the static yield stress [66].

As seen in Fig. 4(a), the static yield stress of PNIPAM-modified cement pastes at 0.15 and 0.3 wt% addition is lower, on average, compared to the Control and the SAP-modified samples. Interestingly, doubling the amount of PNIPAM caused a further reduction in the static yield stress at 30 min after the addition of water to the cement paste. This behavior can be attributed to the absorption and desorption behavior of the PNIPAM particles, as shown in Figs. 2 and 3. PNIPAM exhibits a reduced swelling capacity in general, and its thermo-responsive behavior in a heated solution causes a release of the fluids that it does absorb. Overall, an increase in the effective  $w/c$  ratio due to the thermo-responsive water release can cause a decrease in yield stress and viscosity measurements in cementitious materials [67].

A combination of SAPs and PNIPAM (SAP+PNIPAM) was also considered in the rheology experiments to assess whether PNIPAM could lower the static yield stress in SAP-modified cement paste. SAP+PNIPAM were added in a 0.15 wt% of dry cement for each polymer, keeping the total polymer loading constant at 0.3 wt% for comparison for two reasons, namely (1) to determine if a reduction in the amount of SAP improved the static yield stress (*i.e.*, lowered the static yield stress) and (2) to examine the effect of SAPs and PNIPAM in combination. As evidenced in Figs. 4(a) and (b) SAP+PNIPAM experienced a negligible decrease in the static yield stress of samples that contain only SAP or

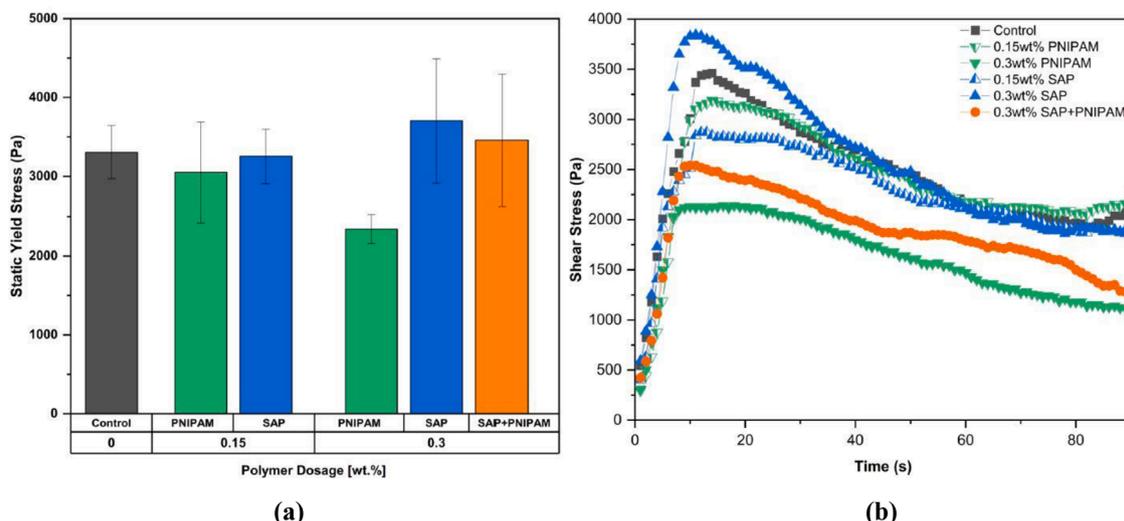


Fig. 4. (a) Static yield stress at 30 min for cement paste modified without and with SAP and PNIPAM hydrogels. Error bars represent  $\pm$  one standard deviation of  $n = 3$  samples. (b) Shear stress versus time at 30 min after addition of water of one representative sample for each mix design.

PNIPAM alone. It is evident from this result that the water absorption behavior of SAPs is the dominant factor in controlling the yield stress of a cement paste, considering that all other factors (polymer size and dosage) remained constant. Additional data on the effects of SAP and PNIPAM on the apparent viscosity of cement pastes at 30 min can be found in the Supplemental Materials (Fig. SM.2.).

### 3.3.2. Influence of polymer on the solid-like behavior of fresh cement pastes

Stress growth measurement tests were performed at various resting periods to characterize the solid-like behavior evolution of cement pastes modified without and with polymers. Increases in static yield stress with time can be represented as thixotropy, which corresponds to hydration and workability loss in cement paste [65]. The static yield stress also corresponds to the critical stress associated with the initiation of the flow of a cement paste initially at rest. Therefore, the static yield stress can be associated with the transition of the cement paste from a solid-like material to a liquid.

Fig. 5 shows the evolution of static yield stress measurements after resting for a time of 10, 15, and 30 min. The static yield stress increases for all samples over time from 10 to 30 min, as expected, due to the formation of some very early hydration products. All samples exhibit similar static yield stresses at 10 and 15 min, which could be attributed to a rest period between measurements that was too short for the cement paste to undergo a significant increase in the amount of structural build-up. It can be observed that the addition of 0.3 wt% PNIPAM exhibited the lowest static yield stress development of all cement pastes. This result could be attributed to the lower thixotropic behavior of PNIPAM, which corresponds to a lower required stress to initiate flow and, thus, improved workability.

SAP-modified samples with the highest polymer dosage of 0.3 wt% exhibit the highest overall static yield stress during the entire testing time (Fig. 5). 0.15% SAP-modified samples and 0.3% SAP with PNIPAM exhibit nearly identical behavior in static yield stress development (Fig. 5). Results again substantiate that SAPs are the dominant factor in

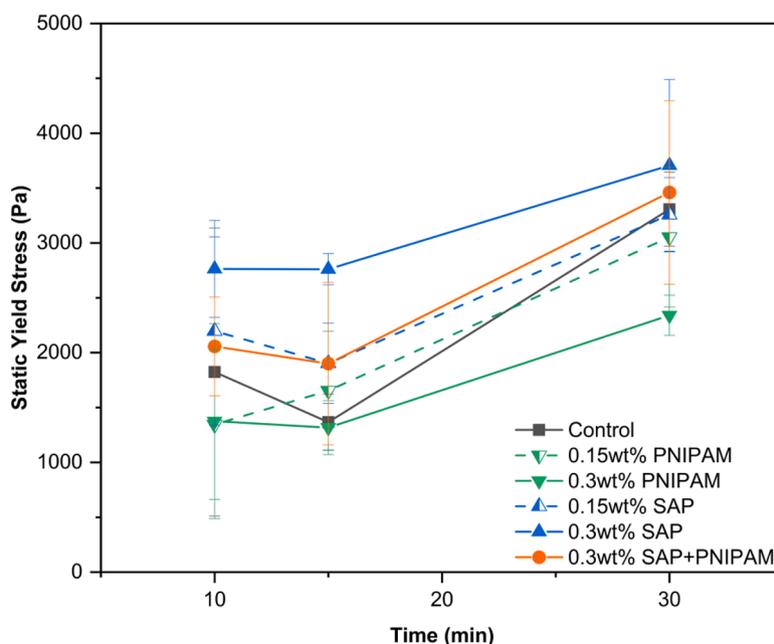


Fig. 5. Static yield stress development of cement pastes without and with SAP and PNIPAM.

determining the rheological behavior, given that SAP-modified samples exhibit high values of static yield stress.

### 3.4. Autogenous shrinkage

Fig. 6 shows the results from 14-day autogenous shrinkage measurements for cement pastes containing SAPs and PNIPAM as well as a Control sample with no polymer addition. Measurements began at the time of the final set (Day 0) and were recorded for 14 days. As previously shown in literature, SAPs reduce autogenous shrinkage, to the point of expansion, in cement pastes for the first 7–14 days [6,14,68]. This expansion can be attributed to void formation once the SAPs desorb their fluid into the surrounding cement matrix [68]. The SAPs studied herein cause a net expansion of the cement paste with a maximum strain of 0.6 mm/m at 14 days. PNIPAM-modified paste experiences a negative strain of  $-0.13$  mm/m at one day and  $-0.85$  mm/m over the course of 14 days compared to the Control sample with a strain of  $-0.13$  at day 1 and  $-1.2$  mm/m at 14 days. These results manifest as improvements of 0.35 mm/m in autogenous shrinkage of PNIPAM-modified paste compared to the Control over the 14-day testing period. The combination of SAPs and PNIPAM shows a maximum positive expansion of 0.07 mm/m for the first day, then a negative strain beginning at day 3 until day fourteen. The maximum negative strain for SAP+PNIPAM was  $-0.48$  mm/m. The overall strain is less than that of the Control sample or samples that contain PNIPAM alone. Based on the results obtained herein, it is likely that higher dosages of PNIPAM alone would lead to further improvements in autogenous shrinkage.

### 3.5. Significance

While the use of SAPs imparts many benefits to cement paste and concrete, their use also introduces some challenges. Prescribed methods for the addition of SAPs in cementitious systems to mitigate autogenous shrinkage or freeze-thaw damage rely on numerous properties of the polymer, including chemical composition and swelling capacity, which can be difficult and time-consuming to quantify based on how the SAP was acquired (*i.e.*, commercially available vs. synthesized in-house) [11, 69]. In addition, while the benefits of SAPs improve the durability of the cement paste or concrete, the adverse effect on workability is

substantial. The recommendation from current research is to add superplasticizers or additional mixing water to compensate for the loss in workability, which, in turn, could lead to reductions in compressive strength if additional water is not correctly accounted for [21,70].

We investigated an alternate approach to modifying the workability of low  $w/c$  cement pastes using non-superabsorbent, thermo-responsive PNIPAM hydrogel particles. A systematic methodology was employed in this study to quantify the swelling behavior, early-age cement hydration properties, rheological behavior, and autogenous shrinkage mitigation potential of a biobased SAP and PNIPAM. The mixtures evaluated herein show that the addition of PNIPAM can improve workability loss in SAP-modified cement paste. Unlike SAP, PNIPAM does not exacerbate water demand by absorbing large amounts of mixing water in the very early ages during which the ionic concentration is low. Time of set and the kinetics of cement hydration were also minimally affected by the use of PNIPAM. Additionally, we found that the use of PNIPAM does offer improvements in autogenous shrinkage strain over the Control paste with an identical  $w/c$  after 7 and 14 days.

Future studies should address the limitations of the use of PNIPAM and explore synergistic avenues for its beneficial use in concrete. The use of PNIPAM should be further investigated to determine the maximum dosage that can be used in cementitious materials. While PNIPAM does provide a significant reduction in autogenous shrinkage, SAP outperforms PNIPAM in autogenous shrinkage mitigation. Thus, increasing dosages should be studies to provide further evidence of autogenous shrinkage improvements. There are likely interactions with supplementary cementitious materials or other chemical admixtures that are yet unknown but should be investigated. Furthermore, commercially available and in-house synthesized SAPs have shown self-healing capabilities in concrete [20,71–73], and to date, there have been no studies to show that PNIPAM can provide self-healing properties to concrete, which warrants further investigation.

This study provides experimental evidence that suggests that utilizing hydrogels as an internal curing agent may not necessarily require the use of ultra-high, superabsorbent hydrogels. The ultra-high swelling capacity of SAPs in the first few minutes of mixing, where ion concentrations can be lower, causes the SAPs to absorb significant amounts of mixing water, causing early-age stiffening. This water is subsequently released as the complexation of SAPs with  $Ca^{2+}$  ions causes collapse of

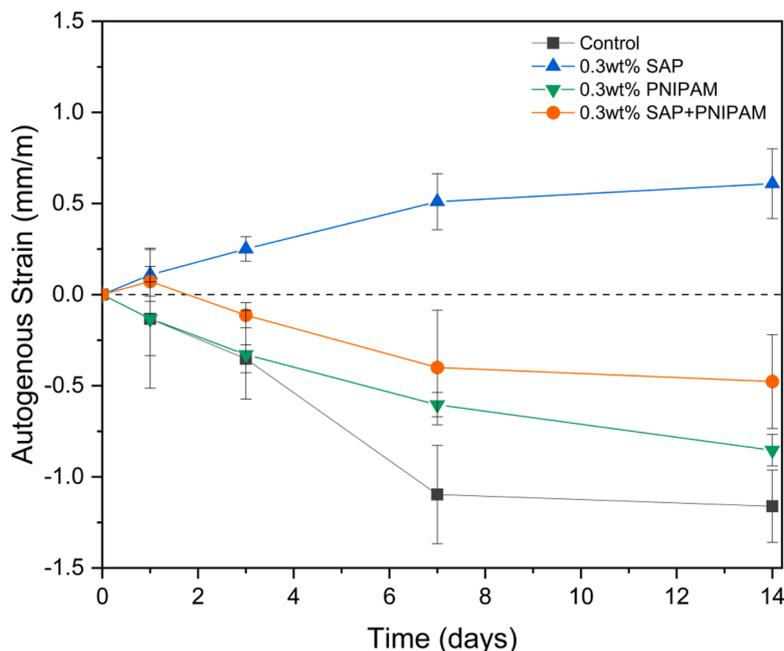


Fig. 6. Autogenous shrinkage strain measurements of cement paste with SAPs and PNIPAM. Dashed line represents zero strain. SAP, PNIPAM, and SAP+PNIPAM samples contain polymer at 0.3 wt%. Error bars represent  $\pm$  one standard deviation of  $n = 3$  samples.

the polymer network and lowers the effective swelling capacity of SAPs to a level comparable to PNIPAM (Fig. 1). Because PNIPAM is not superabsorbent, the negative effects on early-age stiffening are avoided (Figs. 4 and 5), while some later-age benefits of reducing autogenous shrinkage are maintained (Fig. 6).

Chemical (dry or liquid) admixtures play a fundamental role in the concrete mix design. The development of novel admixture chemistries and mechanistic understanding of how they interact with water, cement, and other admixtures is vital in formulating the appropriate mixture design for a given application (e.g., maintaining workability, mitigating shrinkage, ensuring freeze-thaw durability). As evidenced by the data presented in this study, together with other advances in developing new admixture chemistries from chemical [74] and biological [75–77] perspectives, innovations in non-superabsorbent hydrogel admixture technologies offer fruitful opportunities for improving the performance of cement paste and concrete in the fresh and hardened state.

#### 4. Conclusions

In this work, we illustrate that the use of hydrogels as an internal curing agent may not necessarily require the use of ultra-high, superabsorbent polymers (SAPs). This study shows that SAPs play a critical role in water demand, which negatively affects the early-age rheological properties of low w/c cement pastes. The utilization of thermo-responsive non-superabsorbent PNIPAM hydrogel particles with a lower pure water swelling ratio and a tunable LCST (~30 °C) could provide a temperature-controlled release of mixing water without imparting the negative effects of early-age stiffening, as evidenced by the swelling and rheological data reported herein. Dosages of 0.3 wt% PNIPAM reduced the static yield stress over time, thereby improving the workability of cement pastes with a w/c = 0.35. The addition of PNIPAM overcame the adverse effects of SAPs by improving workability in cement paste and exhibits no change in the time of set compared to the Control cement pastes. Through the use of an acrylamide-based hydrogel with non-superabsorbent sorption properties, we show that the water demand induced by the addition of PNIPAM is lower than that of SAPs, while still providing some internal curing benefits to reduce autogenous shrinkage strain.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cement.2022.100049.

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