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Interactions between superabsorbent polymers and cement-based composites incorporating colloidal silica nanoparticles

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ABSTRACT

The relatively new applications of superabsorbent polymers (SAPs) in cement based materials call for investigations regarding their behaviors in relation to other constituents in the system. Colloidal silica nanoparticles (CS) are becoming increasingly important for the improvement of strength and durability of cement based materials. In this study, a poly (AA-*co*-AM) SAP was synthesized by free radical polymerization, and its behaviors in cement based composites incorporating CS were investigated. These included swelling behavior, setting time, mechanical performance in different curing conditions, and rheological properties of fresh pastes. The observation of an unusual reduction in swelling, revealed the role of SAP in precipitation of calcium carbonate from the cement paste filtrate, and provided evidence for the less than expected reduction in workability and setting times. Combinations of the SAP and CS increased the compressive and decreased the flexural strengths, respectively, which is supported by changes in the microstructure as observed by SEM.

1. Introduction

Superabsorbent polymers are hydrophilic crosslinked networks, which can usually absorb and retain very large amounts as high as 5000 times with respect to their own weight of water or aqueous solutions [1]. Based on their origin, three types of SAP can be produced: full synthetic, natural, and hybrid (i.e. grafting synthetic monomers on natural backbone) [2–4]. However, most of the current superabsorbents are synthetic and have an ionic structure. They are most frequently produced from acrylic acid (AA) and its salts, and acrylamide (AM) via solution or inverse-suspension polymerization techniques. The preparation method, monomers, crosslinkers and initiators that are utilized for preparation of the SAP determine the important functional features of the product, such as equilibrium absorption in pure water, absorption under load (AUL), and the rate (kinetics) of absorption.

Commercial SAPs are generally utilized in disposable diapers, sanitary towels, and in agriculture. Other applications of the SAP include contact lenses, tissue engineering, and drug-delivery systems, which have a relatively small share of the total consumption. A less known but commercially important application of the SAP is in the field of construction chemicals. SAP has long been used in the formulation of waterproof backfilling materials, extruded polymeric joint sealants, pre-cooling placement system for concrete, and manufacture of precast products [5–7]. In recent years, SAP has found interesting applications like strengthening of aluminate concrete [8], internal curing of concrete [9], in situ formation of the SAP as a method for repairing cracks [10], and increasing sulfate resistance of concrete [11]. Pioneering theoretical and experimental works by Jensen and Hansen [12,13] were followed by other researches which demonstrated that using SAP in concrete has several benefits such as reduced autogenous shrinkage [14,15] and cracking [16,17], and improved hydration [18–20] of the ordinary cement matrix, as well as the high strength and ultra high strength [21], high performance [22], and ultrahigh performance [23] mixes.

A few studies about other aspects such as visco-elastic properties [24], rheological and hardened properties [25], and the properties in expansive concrete systems [26] were previously reported. However, minimal data is available regarding other aspects of application of the SAP in cement based materials, such as possible interactions with additives and constituents other than cement.

Silica nanoparticles as the most commonly used nanoparticles in concrete, are becoming an increasingly important component of special concretes and other advanced cement based materials [27–30]. They cause great enhancement in compressive and flexural strength, durability, modulus of elasticity, viscosity, and setting time of cement based materials, which is basically due to their reaction with calcium hydroxide and formation of calcium silicate hydrate, and different mechanisms have been proposed for their mode of action [31,32].

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Obviously, the presence of SAP reduces the mechanical performance of cement composites due to the voids introduced in the matrix after deswelling of SAP particles. On the other hand, according to above mentioned paragraph, CS nanoparticles can enhance the properties of cement-based materials by their super-pozzolanic reaction. Furthermore, because the internal curing provided by SAP could change the humidity condition in cement matrix; it was anticipated to affect the reaction of CS with calcium hydroxide and formation of C—S—H.

Another aspect of concern was that CS and SAP have individual negative effects on flowability of cement based composites, but there was a possibility for synergistic effects which could limit their simultaneous usage. Therefore, it was desirable to study the interactions of SAP internal curing agent with the matrix of cement-based material containing CS.

In the present study, the interactions of a crosslinked poly(AA-*co*-AM) SAP with cement pastes incorporating various dosages of the CS was examined. Although both powder form and colloidal dispersion of silica nanoparticles in water are available, the latter is the most convenient and the safest in handling and consumption, and therefore chosen in this work. The swelling behavior of the SAP and its interactions on physical properties, mechanical performance, rheological parameters and microstructure of the hardened cement pastes are investigated.

2. Experimental

2.1. Materials and equipment

Acrylic acid (AA), acrylamide (AM), *N,N′*-methylenebisacrylamide (MBA), sodium hydroxide, and ammonium persulphate (APS) were all purchased from Merck and used without further purification. Double distilled water was utilized in synthesis of the SAP, and tap water was used in preparation of the cement pastes. Colloidal silica nanoparticles and Portland Cement Type I ASTM C150 were purchased from local manufacturers, and their physicochemical properties are illustrated in Table 1. Artificial pore solution was prepared according to [13] with the following composition [mM]: $[Na^+] = 400$, $[K^+] = 400$, $[Ca^{2+}] = 1$, $[SO_4^{2-}] = 40$, $[OH^-] = 722$. Cement paste filtrate was obtained by filtration of cement slurry with Whatman No. 6 filter paper through a Buchner funnel under vacuum.

Minislump spread was measured using a cone with a bottom diameter of 38 mm, a top diameter of 19 mm, and a height of 57 mm. A modified Marsh cone with a height of 310 mm, larger diameter of 155 mm, smaller diameter of 8 mm, and nozzle length of 60 mm was utilized to measure the flow time of the first 500 mL of 1000 mL specimens of pastes. Initial and final settings were measured employing a vicat apparatus according to ASTM C191. Scanning electron microscopy (SEM) images were obtained on a "Philips XL30" instrument applying a test voltage of 15 kV on dried samples coated with gold. FT-IR spectra were recorded on an ABB Bomem MB-100 spectrophotometer with resolution of 4 cm^{-1}. Uniaxial compressive strength was measured on 50 mm cubes and flexural strength was measured using 40 × 40 × 160 mm prisms in three-point bending.

Table 1
Physicochemical specification of cement and colloidal silica nanoparticles.

	Cement	CS
Chemical composition	*wt.%*	*wt.%*
SiO_2	21.4	99.7[a]
CaO	64.1	–
Al_2O_3	4.8	–
Fe_2O_3	3.4	–
MgO	2.7	–
SO_3	1.6	–
$Na_2O + K_2O$	0.6	–
LOI	0.8	–
Physical properties		
Specific gravity (g/cm^3)	3.10	1.32[b]
Specific surface (m^2/g)	0.31	135
Average particle size	21 µm	34 nm

[a] Based on dry matter.
[b] As received (~40 wt.% solid).

2.2. SAP synthesis and characterization

Acrylic acid (12 g) and acrylamide (8 g) were respectively dissolved in 50 mL of water degassed by purging nitrogen, and placed in a 300 mL reaction vessel. Solutions of 2.7 g NaOH in 30 mL water, and 0.086 g MBA in 10 mL water were added slowly, and the temperature was increased to 70 °C. Gelation occurred within a few minutes after addition of 0.127 g APS dissolved in 10 mL water, to the reaction mixture. The reaction was continued for 30 min; subsequently the product was dehydrated with ethanol, scissored to small pieces, and oven dried at 50 °C for 24 h. Next, it was crushed by a rotary disk mill and passed through a series of standard sieves from 40 to 80 mesh sizes, and the fraction under 80-mesh sieve was used in the preparation of cement pastes. The particle size analysis of this fraction and that of Portland cement is displayed in Fig. 1.

The fraction between 40 and 60 mesh was used for measurement of equilibrium swelling, AUL, and kinetics of absorption of the SAP according to the procedures which can be found in detail elsewhere [33]. The swelling media was distilled water, artificial pore solution, 0.9% NaCl solution, and cement paste filtrate. In addition, the equilibrium swelling was measured by an alternative method in which a filter paper was placed at the bottom of a beaker, a weighed amount of the SAP sprinkled on it, and covered with another filter paper. Afterwards the cement paste was poured directly on the top paper, and the whole assembly was covered to prevent evaporation. After 10 min, the beaker turned upside down, and the swelled SAP was quickly collected and weighed to 0.01 g. The swelling (S) was calculated from following equation:

$$S = \frac{w_2 - w_1}{w_1} \qquad (1)$$

where w_1 and w_2 are the weight of the dry and swollen SAP, respectively.

Furthermore, complementary measurements were performed on the kinetics of deswelling of the water-swollen SAP in artificial pore solution, and cement paste filtrate, to obtain a more clear idea about the effect of the order of mixing of constituents on the swelling behavior of the SAP in cement paste.

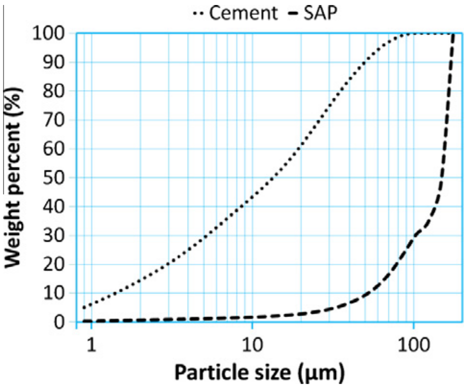

Fig. 1. Particle size analysis of SAP and cement.

Table 2
Mix proportion, compressive and flexural strengths, setting time, Marsh cone flow time and Minislump spread of experimental mixtures.

Mix no.	CS (wt.%)[a]	SAP (wt.%)[a]	Compressive strength (MPa)				Flexural strength (MPa)		Setting time (min)		Marsh cone flow time (s)	Minislump spread (mm)
			Water curing		Room curing		Water curing					
			7 days	28 days	7 days	28 days	7 days	28 days	Initial	Final		
A_0	0	0	28.26	43.35	24.91	35.05	5.9	6.5	410	480	21.4	90
A_1	0	0.1	27.90	43.30	26.34	39.43	5.5	6.2	403	477	22.1	88
A_3	0	0.3	27.37	41.88	27.15	41.57	5.0	6.0	396	470	24.5	85
B_0	0.5	0	28.28	44.65	26.35	36.92	6.1	6.6	–	–	23.4	89
B_1	0.5	0.1	28.72	43.91	28.95	41.45	5.7	6.3	–	–	24.9	86
B_3	0.5	0.3	29.04	43.10	30.65	45.18	5.2	6.2	–	–	28.1	83
C_0	1	0	36.20	48.99	27.95	39.82	6.4	6.9	399	463	30.3	87
C_1	1	0.1	35.98	47.02	29.80	43.32	5.8	6.5	391	460	32.6	84
C_3	1	0.3	32.75	46.25	32.95	47.06	5.6	6.3	386	456	36.3	80

[a] Relative to the total binder.

2.3. Mixture composition and test methods

A series of nine mixtures were prepared according to Table 2. The water to binder ratio (w/b) in all pastes was set to 0.45 to allow for sufficient workability without the need for superplasticizers, thus avoiding any interference and complication in the results. The levels of CS (0, 0.5, 1 wt.% of binder) and the SAP (0, 0.1, 0.3 wt.% of binder) were selected to be well within the safe intervals of their usual dosage. The mixing procedure was carried out according to the following steps:

(1) 3/4 of mix water was put into a rotary mixer, and CS (if any) was added and mixed at 285 rpm for 2 min.
(2) Cement was added in 1 min, while mixing at 140 rpm and mixing continued for another 1 min.
(3) The mixer was stopped for 15 s. The walls were scraped, and mixer restarted at 140 rpm.
(4) SAP (if any) was added in 45 s, and mixed for another 1 min.
(5) The mixer stopped for 15 s. The walls were scraped, and mixer restarted at 140 rpm.
(6) The remaining 1/4 of mix water was added in 15 s, and mixing continued for 4 min.

Marsh cone flow time, Minislump spread, and setting time were measured, and the cubes and prisms for compressive and flexural strengths were immediately cast. The specimens were demolded after 24 h and placed in lime water at 23 ± 2 °C (wet curing), or stored at room conditions with a relative humidity of 30% and the temperature of 23 ± 2 °C (room curing) for two different ages (7 or 28 days). Subsequently, they were tested for compressive and flexural strength according to ASTM C109 and ASTM C348, respectively.

After performing compressive strength measurements in 28 days, a number of pieces were placed into an acetone tank for 48 h in order to stop the hydration reaction; afterwards, they were placed in an oven at 50 °C for 24 h. Next, they were removed from the oven and were cooled in a desiccator for later uses in SEM imaging.

3. Results and discussion

3.1. SAP characterization

Equilibrium swelling of the SAP was examined in different media, and the results are shown in Fig. 2. It is common knowledge that the driving force for swelling of the SAPs with anionic structure is the repulsion between negatively charged groups of the polymer network as well as the osmotic pressure between exterior and interior of the SAP particles. Therefore, the maximum equilibrium swelling takes place in distilled water due to the highest possible difference in osmotic pressure.

Upon increasing ionic strength of the solution, a large reduction in swelling is usually observed, partly because of the reduction in osmotic pressure, and further as a result of charge screening effect [1]. This is due to the presence of the monovalent cations such as Na^+ and K^+ in solution and cause an imperfect anion–anion electrostatic repulsion. Multivalent cations such as Ca^{2+}, Mg^{2+}, and Al^{3+} cause a more severe reduction in swelling due to their complexation with anionic carboxylate groups and forming physical crosslinks in the polymer network [34]. The 0.9% NaCl solution and the strongly alkaline artificial pore solution contained sufficiently high concentrations of monovalent cations; therefore, the equilibrium swelling of the SAP was reduced from 435 g/g in distilled

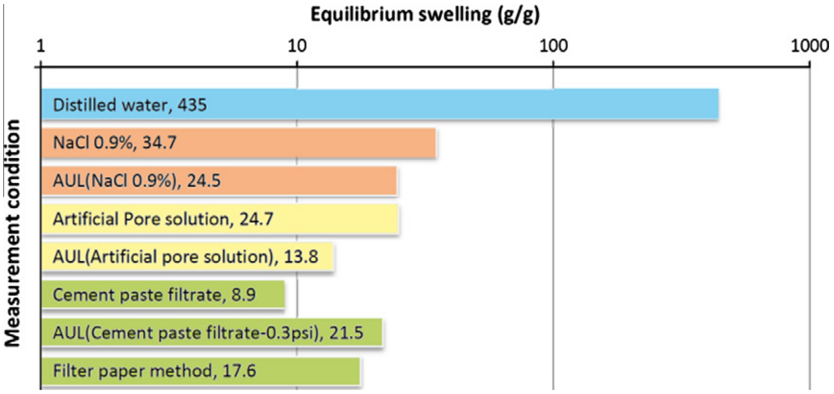

Fig. 2. Equilibrium swelling of SAP measured in different conditions.

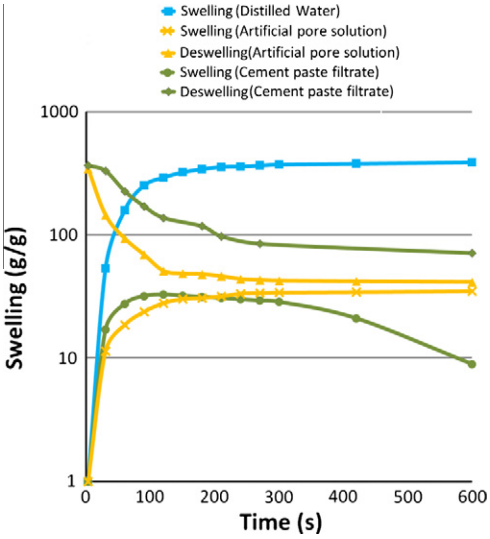

Fig. 3. Kinetics of swelling of dry SAP, and de-swelling of water-swollen SAP upon immersion in artificial pore solution and cement paste filtrate.

water, to 34.7 g/g and 20 g/g, respectively, due to the strong charge screening effect. At first glance, it was not surprising that the absorption of cement paste filtrate by SAP was only 8.9 g/g since it can be justified by assuming a much higher concentration of Ca^{2+} in cement paste filtrate compared with the artificial pore solution. However, the measurements of AUL revealed an unusual behavior of SAP in the cement past filtrate. AUL has become a common test for superabsorbents used in agriculture. In this test various pressures (e.g. from 0.3 to 0.9 psi) and salts solutions (usually 0.9% NaCl) are used to mimic the conditions encountered by the superabsorbent in soil [33]. The swelling of the SAP in concrete also takes place under a load, but the ionic composition is quite different from soil. Therefore, it was necessary to measure AUL using cement paste filtrate and artificial pore solution, in addition to the usual 0.9% NaCl solution. The results of AUL measurements in 0.9% NaCl solution and the artificial pore solution revealed a respective decrease of nearly 30% and 44% compared with the free swelling in corresponding solutions. Surprisingly, the results of AUL in cement paste filtrate and the alternative "filter paper" method presented in Fig. 2 indicate 142% and 97% higher swellings, respectively, compared with the free swelling in the same solution. To the best of our knowledge, this phenomenon has not been previously reported. The reason behind this reversal of swelling behavior was realized during the determination of the kinetics of absorption. Swelling of SAPs generally follows first-order kinetics and can be expressed at any given time by the following equation:

$$S_t = S_e(1 - e^{-t/\tau}) \tag{2}$$

where S_t (g/g) is swelling at time t; S_e is the equilibrium swelling (power parameter, g/g); t is the time (min) of swelling; and τ (min) is the rate parameter. The order of decreasing absorption rate was found to be: distilled water > artificial pore solution > cement paste filtrate that is shown in Fig. 3, respectively.

Although the kinetics and equilibrium swelling in artificial pore solution supported the observations made by other researchers [35], the curve of absorption in cement paste filtrate depicted a peculiar trend, with a steep initial swelling, a maximum swelling of about 32.8 g/g reached in 2 min, and a gradual decrease to equilibrium swelling of 8.9 g/g. Upon closer inspection of the process of swelling, it was noticed that the latter stage was accompanied by the formation of white flocs in the solution which slowly precipitated at the bottom of the solution and on the surface of the swollen SAP particles and caused them to deswell quickly. However, this did not occur when measuring the swelling by the alternative "filter paper" method as described earlier and when measuring AUL, where a barrier such as filter paper or sintered glass disk separated the SAP from the bulk of the solution. These flocs were initially anticipated to form by exudation of a soluble fraction from the SAP into the solution, and subsequent reaction with calcium hydroxide. However, the absence of the characteristic bands of carboxyl or amide functional groups in the FTIR spectra of the precipitate (Fig. 4) suggested an inorganic nature for the precipitate. By wet chemical analysis, it turned out to be calcium carbonate and it was confirmed by further comparison of characteristic bands at 3400 cm^{-1}, 1470, 1408 cm^{-1} (υ3), and 875 cm^{-1} (υ2) in its spectra with that of authentic sample of calcium carbonate as shown in Fig. 4. The cause of this rapid precipitation of calcium carbonate could be that the concentration of ions in solution was increased because of the absorption of water by SAP, thus a supersaturation condition was generated. However, the mechanism by which the precipitation of calcium carbonate contributes to the deswelling of the SAP is not well understood yet and further investigation is to be carried out.

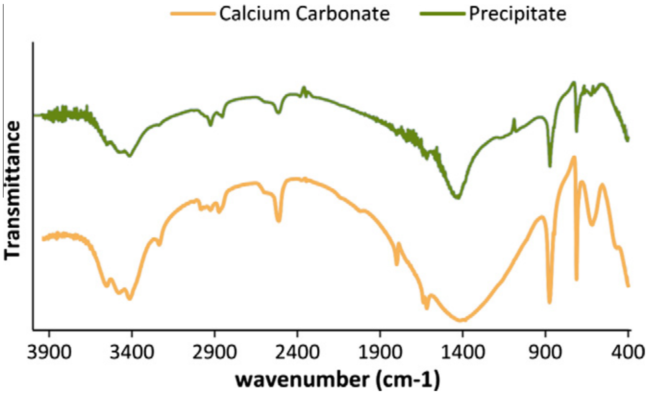

Fig. 4. Comparison of FT-IR spectra of precipitate formed in cement paste filtrate after addition of SAP, with that of calcium carbonate.

The deswelling curve is displayed in Fig. 3, which shows that the kinetics of swelling and deswelling in artificial pore solution had relatively the same pace, and the final equilibrium swellings were quite close. However, this is not true in cement paste filtrate, where deswelling is slower and the final equilibrium swelling is considerably higher compared with that of observed in swelling process. This puts an emphasis on necessity of more investigations about the effects that the order of mixing of ingredients could have on the behavior of the SAP in cement based materials.

3.2. Setting time

Data presented in Table 2 implies that SAP has no significant effect on setting time because the maximum difference between mixes without SAP and their counterparts with 0.3% SAP is 14 min for the initial, and 10 min for the final setting time. The high w/b ratio together with the small dosage of the SAP could give reason for this small effect. Since the higher w/b ratios normally extend the setting time, the difference between final setting times was smaller than the initial setting times probably due to the partial release of water from SAP to cement paste matrix during this period. This was further reflected in minor decrease in setting time between mixes with 0.1% and 0.3% SAP.

The effect of the CS was more pronounced on final setting times and the comparison of mixes without CS and those with 1% CS, both containing the same level of the SAP, were reduced up to 17 min. Therefore, the time lag between the initial and the final setting times of mixes without CS was larger because its presence reduced final setting time more than initial setting time and the addition of the SAP intensified this difference through reduction of initial setting time. To understand the mechanism of reduction in setting time by CS, it should be noted that CS has a large number of unsaturated bonds or free valances on the surface, which are highly reactive. In cement paste matrix, these are in the form of silanol groups and show a high reactivity toward calcium hydroxide and, therefore, a condensed calcium silicate hydrate gel rapidly develops as a result of large specific surface area and high pozzolanic activity of the CS [32]. Another important fact is that adsorption of the CS on the surface of cement particles and between hydration products promotes the hydration reaction [36] due to their high activity, and promotes the setting process.

3.3. Rheological properties

The results of Minislump spread and Marsh cone flow time are shown in Table 2; which represent rheological parameters yield stress and viscosity, respectively. By increasing quantities of the SAP and CS, Minislump spread was reduced and Marsh cone flow time was increased. Since the effect of the SAP on rheology is believed to be through the reduction of free water available in the mix (about 14% of the mix water at the 0.3% level of addition), in fact a much higher reduction in spread was expected. This effect suggested that some compensating mechanism should be at work. An explanation could be the fact that the swollen SAP particles exerted a lubricating effect on the matrix similar to the well-recognized effect of entrained air on increasing the slump of concrete mixes. Another fact that should be taken into account is the rapid deswelling of the SAP in cement paste filtrate due to the precipitation of calcium carbonate, and release of a large amount of the absorbed water. Assuming that the same also occurs in cement paste, it can partly justify the small change in yield stress of the SAP-containing mixes compared with those without SAP.

On the other hand, the addition of the CS caused a considerable decrease in spread and an increase in flow time, mainly because of very high specific surface area and the extensive polar interactions of the negatively charged CS with cement particles that bear a positive charge. By comparing the effects of SAP and CS on rheological parameters, it can be observed that CS mainly affected viscosity, while SAP affected yield stress the most. It is worth to mention that both yield stress and viscosity showed a curvature over the relatively small range of dosage of either SAP or CS, i.e. the slope of increase in flow time or decrease in spread was higher between 0.5–1% CS and 0.1–0.3% SAP. It is especially important to consider this nonlinearity when making a compromise between desirable mechanical performances and unwanted rheological consequences of consumption of these materials.

3.4. Compressive strength

The compressive strength at different ages and curing conditions are displayed in Fig. 5a and b. It is evident that the SAP exhibited contradictory behaviors in different curing conditions; in water curing, higher dosage of the SAP decreased the compressive strength, while in room curing an increase in compressive strength was observed.

The main reason was that in wet curing the hydration reaction of all samples proceeded nearly to the same extent, thus the reduction in strength was proportional to the amount of voids in the matrix after deswelling of the SAP particles. It is known that the main effects of the SAP on structure of cement-based materials include a discontinuous pore structure and an improvement in hydration of cement particles due to the gradual release of water, which maintains a high level of relative humidity [12,13]. Consequently, in wet curing conditions, both the external water supply and internal water provided by SAP participated in improvement of structure; however, considering the small contribution of the SAP, the improvement due to the external water was prevalent and the porosity caused by the SAP became its dominant factor contributing to the strength, therefore this condition resulted in a decrease. On the other hand, when samples were cured at room conditions, the improvement in structure could only be a result of the role of the SAP particles as water reservoirs, which outweighed the negative effects of higher porosity on strength.

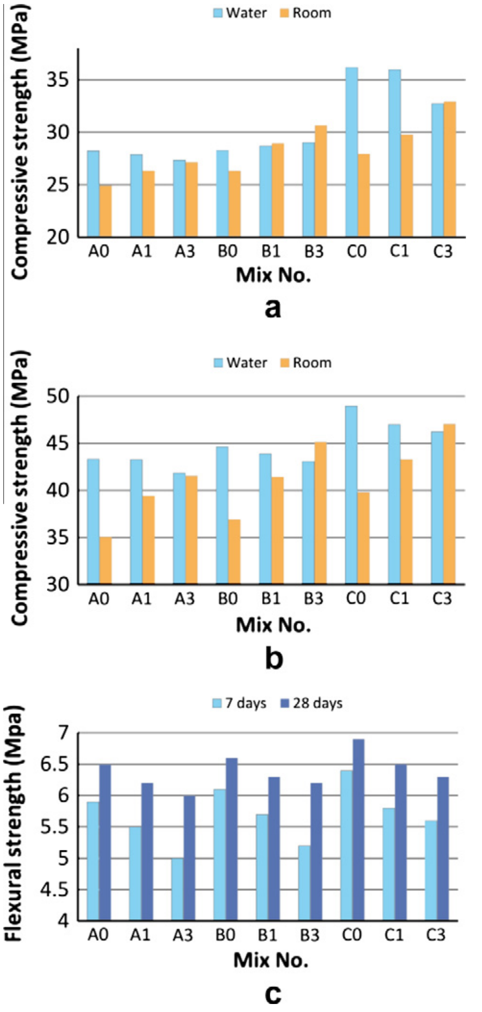

Fig. 5. Compressive strength for room curing and water curing at 7 days (a), 28 days (b), and flexural strength for water curing at 7, and 28 days (c).

The effect of adding CS to the pastes was a steady improvement in compressive strength in different curing conditions because of the improved microstructure of pastes due to the very high pozzolanic reactivity of CS with calcium hydroxide produced during hydration of cement. CS improves the microstructure and macrostructure of cement based composites by a variety of mechanisms including control of crystallization, promotion of hydration reaction, and micro/nano-filling effects [31,32]. However, the formation of a condensed calcium silicate hydrate (C—S—H) gel, according to the following reaction has the greatest contribution to the development of strength and durability in cement based products.

$$2SiO_2 + 3Ca(OH)_2 \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O \qquad (3)$$

It is important to note that the efficacy of the CS in wet curing was higher than that of room curing. This could be explained by the continuing hydration process of cement particles and higher production of calcium hydroxide for pozzolanic reaction of the CS in the presence of additional moisture as well as its promoting effect on the hydration reaction of cement particles as mentioned earlier. In addition, the rate of increase in strength at 7 days was higher than at 28 days, a trend that was not observed in samples cured at room condition. This high early increase in strength could be attributed to the high reactivity and very large specific surface area of CS, which left little unreacted material in later ages, thus the rate of increase in compressive strength was slowed down. In room condition however, it could be proposed that the evaporation of a large part of the mix water caused a reduction in the rate of hydration, and possibly the agglomeration of CS, which in turn could reduce its effectiveness in improving the compressive strength.

In different curing conditions and ages, the addition of the CS to the pastes that were internally cured with SAP, invariably increased the strength relative to the blank mix (A_0). For wet cured specimens containing CS, the addition of 0.1% SAP increased the strengths at 7 days compared with the corresponding pastes without SAP, however this was not true at 28 days. With addition of 0.3% SAP along with CS, the changes in strength at 7 days were inconclusive; on the other hand, higher strengths compared with 0.1% SAP were obtained at 28 days. Once more for room-cured samples, addition of 0.1% SAP improved the strength of CS-containing mixes at 7 days but not at 28 days, compared with the ones without SAP. However, when 0.3% SAP was used, the strength at both ages (7 and 28) were enhanced compared with the corresponding mixes with 0.1% SAP.

Besides the aforementioned effects that SAP and CS had on compressive strength, it was important to investigate the interactions of these two factors with each other and with other experimental variables such as age and curing method. The interaction plot in Fig. 6a is an effective means of visualizing the effects of different combinations of factors on the strength.

In these plots, one could detect interactions among factors simply by differences in slope or curvature of the plots. For example, small differences in slope of the interactions between age and curing method indicated that shifting from room to water curing was slightly more effective at the age of 28 days. The same trend existed for interaction between the age and SAP, i.e. the increasing amounts of the SAP was more beneficial to the strength when paste specimens were cured for 28 days. In addition, other interaction plots could be interpreted accordingly, and it could be observed that the most important interaction corresponding to the highest difference in slopes, was that of the SAP and curing method and indicated that the addition of the SAP caused the greatest increase in strength when the specimens were cured at room condition. Water curing demoted the positive effect of the SAP on strength and in fact, a slight decrease was observed as the amount of the SAP was increased. This is consistent with the results by other researchers [37], although their interpretation of the cause of this decrease could not be supported. It should be noted that the values employed for constructing the interaction plots were the means of the results in which all variables excluding the two under investigation, changed over the experimental space; therefore, the conclusions derived from these plots should be valid over a wider set of experimental conditions.

3.5. Flexural strength

Flexural strengths of the specimens cured in water at different ages (7 and 28 days) are displayed in Fig. 5c. Evidently, the addition of the SAP to the mix caused a large decrease in flexural strength, which was more pronounced compared with the reduction in compressive strength in similar conditions. This meant that the voids produced in the matrix upon addition of the SAP were more detrimental to the flexural strength. However, unlike compressive strength, the magnitude of this negative effect was reduced at 28 days. The presence of the CS increased the flexural strength for the same reasons discussed in previous section and it is noteworthy that the rate of this increase was higher at 7 days. Finally, in the presence of 0.1% or 0.3% SAP, the performance of CS at early age of 7 days was improved accordingly. This trend was somehow different from the behavior of the compressive strength of combinations of the SAP and CS under wet curing conditions.

More information about the interactions among main variables is conveyed in Fig. 6b. The interaction plot between the age and CS showed that the rate of increase in flexural strength between 7 and 28 days became slightly slower when CS was increased. Furthermore, at each age, the effect of addition of 0.5% CS was not halfway that of 1% CS, i.e. the increase of flexural strength was accelerated by increasing the amount of the CS. A similar situation existed for interaction between the age and SAP and although the presence of the SAP reduced the flexural strength; there was a higher rate of increase for the samples containing SAP, as the age increased from 7 to 28 days. Consequently, the effect of 0.1% SAP at each age was closer to that of 0.3% SAP that meant the addition of the first 0.1% SAP caused more decrease in flexural strength than the next 0.2%. Finally, the interaction between the SAP and CS displayed another interesting feature. At 0% and 0.5% additions of CS, a linear decrease in flexural strength was observed with increasing levels of the SAP. The two plots were nearly parallel and there is no

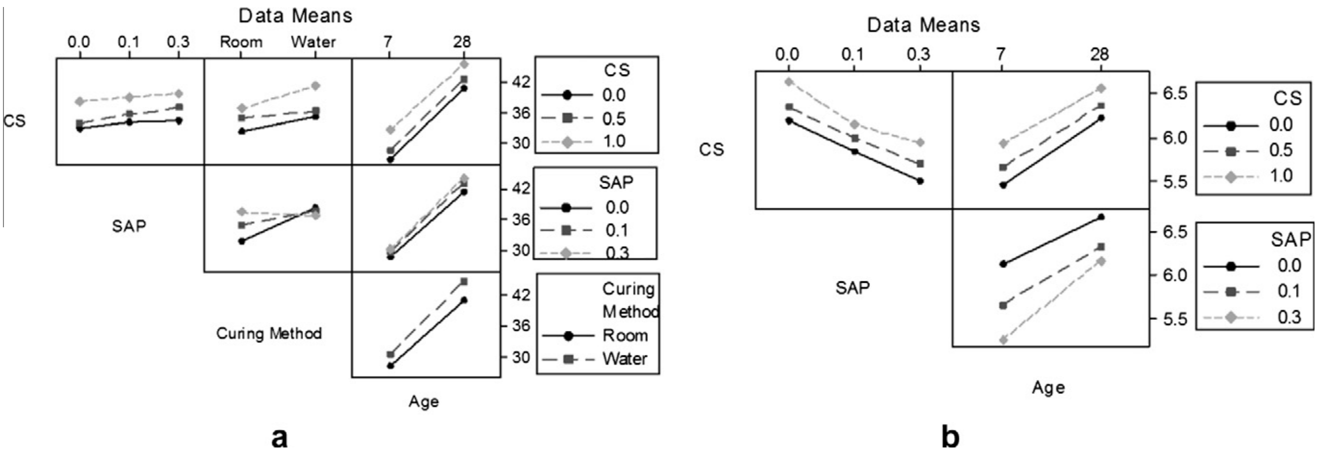

Fig. 6. Interaction plots for compressive strength (a) and flexural strength (b).

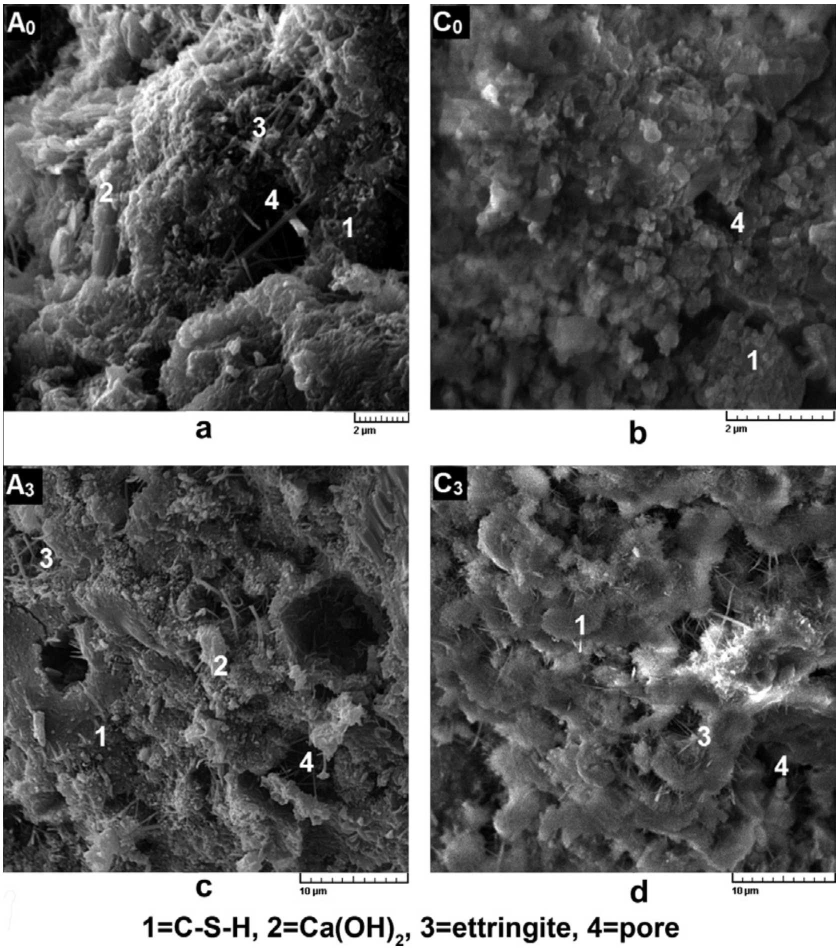

Fig. 7. SEM images of pastes cured at room condition for 28 days: (a) mix A_0 (blank), (b) mix C_0 (1 wt.% CS), (c) mix A_3 (0.3 wt.% SAP), and (d) mix C_3 (1 wt.% CS + 0.3 wt.% SAP).

or little interaction between the SAP and CS. However, when the amount of the CS was increased to 1%, there was a curvature in the plot and obviously the rate of decrease in flexural strength was higher for addition of 0.1% SAP. Further addition of SAP to 0.3% caused a milder decrease in flexural strength. As discussed before, SAP had a negative effect on strength by introducing voids into the matrix, and a positive effect by improving the hydration reaction of cement and pozzolanic reaction. Because the specimens for flexural strength were all cured in water, the changes could not be attributed to the difference in hydration, which suggested that the presence of sufficient amounts of CS simply puts a limit on negative effects of increasing dosages of the SAP.

3.6. Scanning electron microscopy

To evaluate the impact of the CS and SAP and their combination on microstructure of cement pastes, SEM images of four selected specimens (Fig. 7) were obtained after their hydration was stopped as described in experimental section. It was confirmed in Fig. 7a that an extensive and interconnected capillary system was present in control mix (A_0). The microstructures were non-compact and needle-like crystals of ettringite were abundant in vacant spaces, and large crystals of Portlandite were extensively formed as well. The morphology of C—S—H in this mix was fluffy and fibrous, which is the characteristic of cement pastes with high w/b ratio [38]. It is displayed in Fig. 7b that in mix (C_0), the addition of 1% CS reduced the porosity of the hardened cement paste because of super pozzolanic performance and the production of higher amounts of C—S—H gel. In addition, the microstructure was considerably improved due to the micro and nano-filling effects. No ettringite was detected either in the context of C—S—H gel or in the open space of the cracks. Crystals of Portlandite were reduced in size and quantity as a consequence the pozzolanic reaction and crystal growth control by CS. All of the above improvements in microstructure were reflected in the macroscopic properties such as higher mechanical performances of the specimens.

Upon the addition of 0.3% w/w SAP to the mix (A_3) as shown in Fig. 7c, the microstructure of the paste in the vicinity of the SAP particles was obviously improved as a result of more effective hydration of cement particles under the influence of internal curing provided by SAP. This finer microstructure had a nearly distinct border and there was a visible change in microstructure beyond this limit. Furthermore, in (A_3) a higher amount of Portlandite was produced compared with (A_0) and the morphology of C—S—H gel was more condensed, representing a lower amount of free capillary water initially present in the mix. It was noteworthy that the amount of ettringite formation was further reduced. Finally, mix (C_3) contained 0.3% w/w SAP and 1% w/w CS that is displayed in Fig. 7d. There was a denser and finer structure of C—S—H gel than that of observed in Fig. 7b that represented the synergistic effect of combination of SAP and CS on microstructure of the paste. The amount of Portlandite crystals was small and crystals of ettringite were produced to a lesser extent compared with (A_0) and (A_3).

From the above observations, it became apparent that the SAP played an important role in control of Portlandite formation, and further in densification of C—S—H gel through modification of its morphology. However, the presence of CS in the mix caused a finer pore system in the mix by extensive pozzolanic reaction and conversion of Portlandite to C—S—H gel. The combination of the CS and SAP benefited from all of the above functions of individual components in addition to the possibility of more efficient pozzolanic reaction of CS as a result of finer and more controlled production of Portlandite in the paste.

4. Conclusions

The future of superabsorbent polymers as internal curing agent for cement-based materials will be determined by so many other features and not simply by their water absorbing and releasing capability. Even the interpretation and generalization of latter properties should be carried out more cautiously. The equilibrium swelling of the SAP was dependent on the chemical composition of the medium, method of measurement, loading conditions, order of mixing, and probably other variables. It was found that the formation of calcium carbonate precipitate severely reduced the swelling capacity of the SAP. The individual and combined effects of the SAP and CS on physical properties, rheological behavior, mechanical performance and microstructure of cement pastes revealed the following facts about their benefits and limitations:

- Only the swelling of the SAP in cement paste filtrate causes rapid formation of calcium carbonate and a subsequent deswelling, emphasizing that artificial pore solution is not a genuine representative of cement paste environment to evaluate the SAP behavior.
- The influence of the SAP on decreasing spread is more pronounced than on the increasing flow time of the pastes and the reverse is true for CS. The effect of SAP is smaller than what is expected based on water absorption alone; hence, a lubricating effect of the SAP is anticipated to be in charge, possibly together with the reduced swelling as described.
- The importance of internal curing in cement pastes containing CS is reflected both in promotion of the hydration reaction of cement, and pozzolanic reaction of CS with Portlandite especially at room curing and early ages. The net effect of the SAP in pastes is positive regarding the compressive strength and negative regarding the flexural strength. Therefore, flexural strength can be considered a limiting factor in designing mixes containing SAP.
- The major changes in microstructure of the paste due to the presence of SAP are a denser morphology of C—S—H gel, particularly within a certain distance from the particles, and higher production of Portlandite as a raw material for pozzolanic reaction. The main effects of CS on microstructure are considerable reduction in porosity of the capillary system due to the formation of C—S—H, control of crystal growth, and promotion of hydration reaction of cement.

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