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The potential of superabsorbent polymer for self-sealing cracks in concrete

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Abstract

The potential of conventional superabsorbent polymers (SAP) based on partially neutralised acrylate and acrylate/acrylamide copolymers as an admixture for self-sealing of cracks in concrete is investigated. SAP are cross-linked polymers that can absorb a disproportionately large amount of liquid and swell substantially to form a soft and insoluble gel. However, their swelling capacity is highly dependent on the alkalinity and ionic content of the solution. These characteristics may be exploited for self-sealing cracks in concrete. In this preliminary study, the mechanism involved is described and tests performed to determine the swelling ratios of SAP in various solutions including synthetic pore solution, groundwater and seawater are reported. Transport testing found that the flow rate through a 340μm wide model crack is reduced substantially by using less than 1% vol. SAP. The re-swelling capacity of SAP in cement paste and the effect of SAP on cement paste microstructure were investigated by microscopy.

Keywords: Self-sealing, Superabsorbent polymer, Hydrogel, Concrete, Cracking, Durability

1. Introduction

Cracking of concrete structures is a common problem owing to the intrinsic brittleness of the material. Narrow cracks may self-heal[1-3], but larger cracks reduce watertightness and durability. Conventional approaches to mitigating these problems include providing additional reinforcement or movement joints in new structures and resin injection of cracks in existing structures[4]. These methods, although widely used, are not always appropriate or sufficient.

Superabsorbent polymers (SAP) are cross-linked polymers that absorb, swell and retain a large amount of liquid from their surroundings without dissolving. The rate of swelling for small SAP particles ranges from less than a minute to hours depending on the diffusion coefficient and diffusion path length of the polymer[5]. Developed in the late 1960s, SAPs are now widely used in personal care products such as nappies. In 2005, the global production capacity of SAPs was estimated to be about 1.48 million tons[6]. Other applications of SAP include biomedical (bandages, surgical sponges), agricultural (soil conditioning, erosion control), waste solidification, meat packaging and water blocking tapes for undersea cables[5]. In concrete technology, the application of SAP for enhancing strength and workability[7], preventing drying shrinkage cracking and leakage through cracks[8], and internal curing[9, 10] have been proposed.

Conventional SAP is described as anionic acrylic that comprises a copolymeric network based on partially neutralised acrylic acid or acrylamide[11]. The large majority of commercial SAP are of this type. An important characteristic of this type of SAP is that its swelling alters in response to the pH, salinity[12-14] and the concentration of specific types of ions[15, 16] of the solution. For example, its free swelling ratio, which is the water uptake by mass of dry SAP, can be up to 5,000gg^{-1} in deionised water, but reduces significantly with increasing ionic concentration of the solution, e.g. ~50gg^{-1} in urine and ~10gg^{-1} in concrete pore solution[9, 10]. Furthermore, the swollen SAP gel forms a barrier to flow[5, 17], and it is this property that is exploited for sealing cracks.

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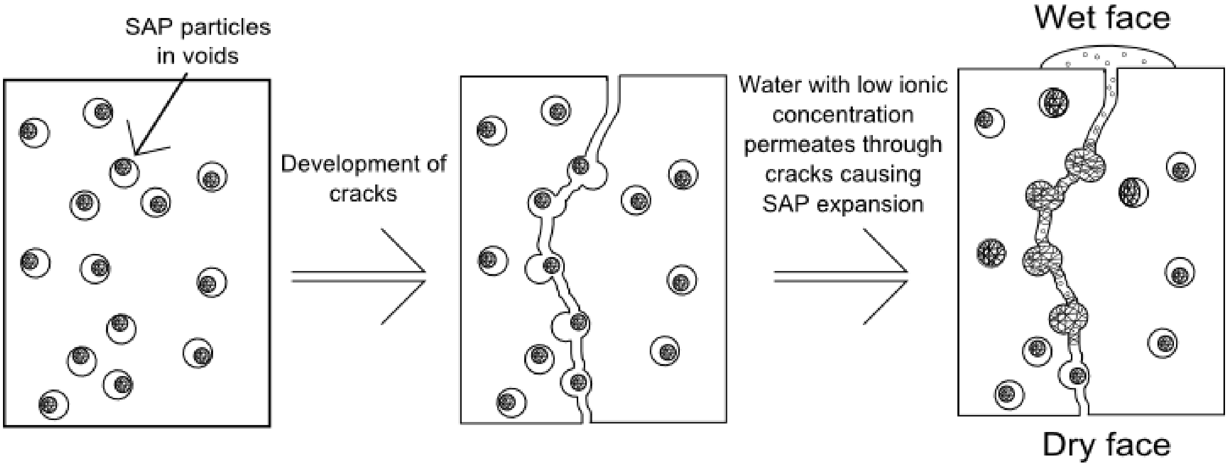
2. Mechanism of self-sealing cracks

The following behaviour is envisaged. SAP is added to the concrete mix, which is cast using conventional methods. At this stage, the SAP swells only slightly because the mix water reaches a high pH (~12.5-13) and high ionic concentration (ionic strength ~ 150 - 700 mmol.l^{-1}) within minutes of being in contact with cement[18]. The calcium ions in the mix water may also form bidentate complex with the acrylates of the SAP[19] which further limits its swelling[20, 21]. As the cement hydrates, the SAP releases water and shrinks, leaving behind pores with sizes ranging from tens to hundreds of microns in the cement paste (Fig. 1a). The size of these pores is similar, if not larger compared to other ‘flaws’ in the cement paste, such as capillary pores, microcracks and the aggregate-cement paste ‘Interfacial Transition Zone’. Therefore, they can be viewed as macro-defects and cracks that form during the service life of the concrete structure are likely to propagate through them (Fig. 1b). When the concrete is subjected to external wetting, ingress of moisture causes the SAP to swell again. If the external fluid has a low ionic concentration, such as in shallow groundwater, the SAP will swell more than in concrete pore solution, hence expanding beyond the pore and into the crack.

External water sources include natural sources such as precipitation, groundwater, or seawater, and processed water as found in pools and tanks. The chemical compositions of these water sources vary widely. Precipitation typically contains 10-20mgl^{-1} of dissolved solid[22]. Groundwater composition, on the other hand, depends on factors such as residence time and the minerals forming the ground[23]. Natural shallow groundwater usually has a low ionic concentration (typically of ionic strength ~ 0.4 - 30 mmol.l^{-1} [23-25]). In these solutions, SAPs should swell significantly. The swollen SAP can then fill the crack and slow down or even prevent further infiltration of water (Fig. 1c). In addition to the direct physical blocking effect of the SAP, the swollen SAP may promote autogeneous healing of cracks by reducing flow rate. These effects would help retain the watertightness of cracked concrete structures.



(a) (b) (c)

Fig. 1 Schematic showing the potential mechanism of self-sealing cracks using SAP

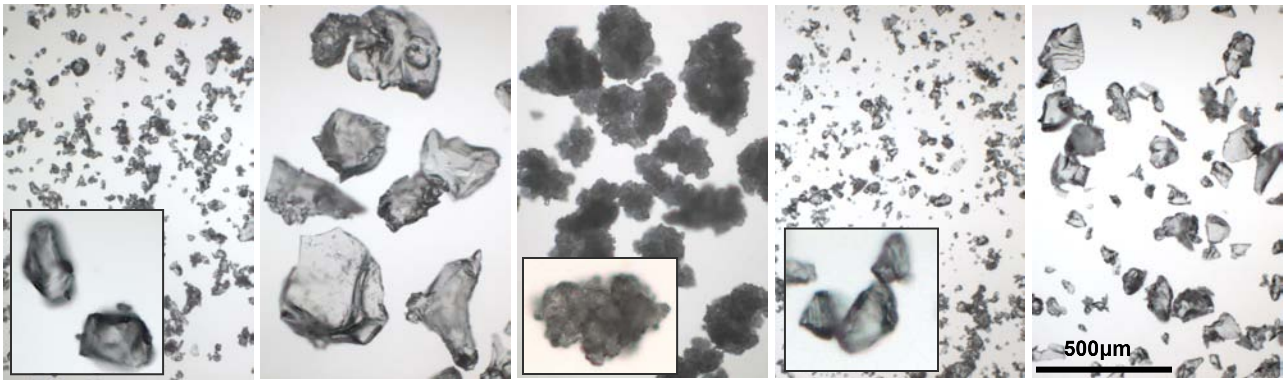
3. Experimental

3.1 Materials

We obtained over twenty commercial SAP samples, from which five were selected and used in this study. The rest were rejected because their particle sizes were far too large for our application. The properties of the SAP, as provided by their respective manufacturers, are listed in Table 1. The selected SAP are either cross-linked sodium polyacrylate (Poly(AA)) or potassium poly(acrylate-co-acrylamide) (Poly(AA-co-AM)). They are in a white powder form with particle size ranging from several microns up to about 500μm. When viewed using an optical microscope in transmitted light, S1, S2, S4 and S5 appear as smooth, angular and irregular shaped granules, and sometimes as convoluted sheets (Fig. 2). S3 has a very rough surface texture and appears to be agglomerates of smaller particles.

SAP	Source	Diameter (µm)	Bulk density (kgm^{-3})	Polymer type
S1	BASF, Germany	<100	600-700	Poly(AA)
S2	Evonik, Germany	100-300	n/a	Poly(AA)
S3	ETi, U.S.A.	100-500	420	Poly(AA)
S4	Evonik	0-90	n/a	Poly(AA-co-AM)
S5	ETi	1-200	540	Poly(AA-co-AM)

Table 1 Properties of the SAP used in this study



S1 S2 S3 S4 S5

Fig. 2 Transmitted light micrographs showing the particle size and shape of the SAP samples used in this study. The images were captured at the same 50x magnification, giving a field of view of ~ 900x1350µm. Insets for S1, S3 and S4 are magnified sections to improve clarity.

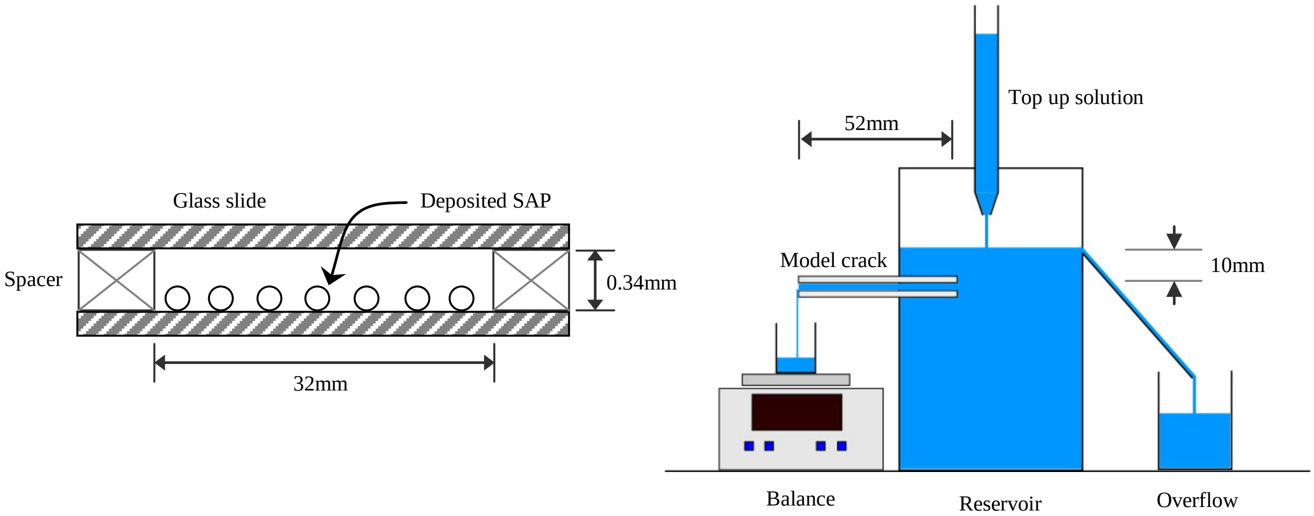
3.2 Swelling ratio

The swelling ratios of the SAP (gg^{-1}) in various solutions were measured using a suction filtration method[15]. 100mg of the SAP (pre-dried at 50˚C) was immersed in 50ml of the solution for 60 minutes at 20˚C to allow the SAP to absorb. The swollen SAP was then filtered by suction (~0.17 bar) over a filter paper for 5 minutes and weighed. The swelling ratio is the water uptake by mass of dry SAP. The test solutions were deionised water, tap water, NaCl (0.12 wt.% and 0.9 wt.%), synthetic shallow ground water, synthetic concrete pore solution and synthetic seawater. The compositions of the solutions are listed in Table 2. A relatively concentrated synthetic shallow groundwater solution (ionic strength = 21 mmol.l^{-1}) is chosen in this experiment so that the swelling ratio obtained from it is likely to be a conservative value. The 0.12wt.% NaCl solution is taken as a simple synthetic shallow groundwater, while the 0.9wt.% NaCl solution is a typical benchmark solution to enable comparison with other studies. Two synthetic pore solutions were tested. Their compositions are based on the pore solution extracted from a cement paste with water/cement of 0.5 within 30 mins of mixing[18]. Their difference in ionic contents is due to the chemical composition of the cement. The effect of repeated wetting and drying on the swelling ratio of two SAP types (S2 & S5) was also investigated. The samples were immersed in 0.12 wt.% NaCl for 24 hours, filtered and weighed, then dried at 50°C for 48 hours. This was repeated for five cycles on each sample.

3.3 Crack sealing

In this experiment, the flow rates of various solutions through a model crack containing SAP (S1) were measured. The cross section of the model and the test set up are illustrated in Fig. 3. The model crack is essentially a slit made with two parallel glass slides (52x76mm), with one containing pre-deposited SAP particles. This was produced by placing the glass slide at the bottom of a tank containing a mixture of de-ionized water and 3-15mg of SAP, and drying at 50°C to allow the SAP to collect on to the glass slide. Spacers made of cover slips were sandwiched between the edges of the two glass slides to form a slit of approximately 0.34mm width, and the two sides of the assembly were sealed with duct tape. About twenty of these model cracks containing various amounts of deposited SAP (up to 1% vol.) were made and tested. The amount of deposited SAP is expressed as the volumetric fraction of the dried SAP to the crack.

Flow measurements were performed using the setup shown in Fig. 3b. A pressure head of 10mm was applied, which generates a small pressure gradient of approximately 0.2 (~1960Pam^{-1}). Attempts to increase the pressure gradient, however, were unsuccessful because a higher pressure tended to expel the SAP from the parallel-sided model crack. The solution that passed through the crack was collected and weighed periodically until a stable flow rate was obtained, which required about 5 to 25 minutes. Moisture lost due to evaporation was corrected. Tests were performed using tap-water, 0.12 wt.% NaCl, synthetic shallow groundwater and seawater as the permeating fluids.



(a)

(b)

Fig. 3 Schematics showing a) cross section of the model crack containing deposited SAP, and b) set up for measuring flow through the model crack (not to scale).

3.4 Microscopy

Neat cement paste samples containing OPC and 1% SAP (by wt. of cement) at water/cement ratios of 0.36 and 0.50 were prepared for optical and backscattered electron microscopy. The cement and SAP were dry mixed initially to disperse the polymer particles, before adding distilled water. The pastes were cast into small blocks (50x25x10mm) and sealed cured in cling film for 5 days at room temperature. For optical microscopy, the blocks were ground using silicon carbide paper to produce a flat surface and to expose the SAP. They were then ultrasonically cleaned in acetone for 30 seconds and dried at 50°C for 24 hours. For backscattered electron microscopy, the blocks were dried at 50°C for 3 days, then impregnated with a low viscosity epoxy and polished down to a 1μm finish. The polished blocks were carbon coated and observed using a field-emission SEM.

4. Results

4.1 Swelling ratio

The swelling ratios of SAP in the various solutions are given in Table 2. As expected, the swelling ratio is the highest in deionised water, followed by tap water and generally decreases with increasing ionic concentration of the solution. The swelling ratios of SAP in synthetic shallow groundwater and 0.12% NaCl solution are quite similar, but significantly higher (about 4 to 28 times greater) than in the ‘weak’ synthetic pore solution. This supports the idea that SAP cast in concrete has the potential to swell beyond its original boundary to block cracks. It is also interesting that the swelling ratios in the ‘strong’ synthetic pore solution are higher than that in the ‘weak’ pore solution, particularly for S3. This is probably because the significant increase in the concentration of monovalent cations in the ‘strong’ synthetic pore solution reduces the formation of swelling-prohibiting bidentate complex by displacing the Ca^{2+} from the acrylate chain[20]. However, the lower swelling in synthetic seawater suggests that this self-sealing approach is unlikely to be applicable to marine structures.

Table 3 gives the swelling ratios of S2 and S5 obtained after repeated wetting in 0.12% NaCl and drying at 50°C for up to five cycles. The results show that the swelling ratio is fairly consistent for each cycle, indicating that the SAP can re-swell after drying with no apparent deterioration in its swelling capacity. Obviously this is a desirable property if SAP is to be used for crack sealing.

Solution	Composition, ($mmol.l^{-1}$)	Swelling ratio, $g.g^{-1}$ *				
		S1	S2	S3	S4	S5
Deionised water	-	214 (*36*)	222 (*15*)	259 (*86*)	313 (*16*)	208 (*11*)
Tap-water	-	80 (*13*)	109 (*7*)	123 (*41*)	96 (5)	97 (*5*)
0.12 wt.% NaCl	NaCl (20)	77 (*13*)	79 (*5*)	82 (*27*)	87 (4)	73 (*4*)
0.9 wt.% NaCl	NaCl (153)	37 (*6*)	31 (*2*)	33 (11)	33 (2)	27 (1)
Synthetic shallow groundwater [26]	$NaHCO_3$ (8.2), $CaSO_4$ (1.04), $MgSO_4$ (2.08) & $CaCl_2$ (0.14)	64 (*11*)	89 (*6*)	85 (*28*)	89 (4)	71 (*4*)
Synthetic pore solution (weak)[18]	$CaSO_4$ (17.6), KOH (25), NaOH (10)	6 (*1*)	15 (*1*)	3 (*1*)	20 (*1*)	19 (*1*)
Synthetic pore solution (strong)[18]	$CaSO_4$ (20.6), K_2SO_4 (163.4), KOH (71.2), NaOH (73.9)	16	21	22	29	23
Synthetic seawater[27]	NaCl (489), $MgCl_2$, (41), $MgSO_4$ (15), $CaSO_4$ (9.6), K_2SO_4, (5)	4 (*0.6*)	2 (*0.1*)	2 (*0.7*)	13 (*0.7*)	11 (*0.6*)

* Value in brackets is the swelling ratio normalised to that of the ‘weak’ synthetic pore solution

Table 2 Swelling ratios of SAP in various solutions

SAP	Swelling ratio, $g.g^{-1}$					Average	Standard deviation
	1	2	3	4	5		
S2	79.6	80.3	81.6	81.7	85.4	81.7	2.2
S5	78	73.5	77.7	79.1	78.1	77.3	2.2

Table 3 Effect of repeated wetting with 0.12% NaCl and drying at 50˚C on the swelling ratios of S2 and S5

4.2 Crack sealing

The results of the transport tests are shown in Fig. 4. The flow rate through the crack model containing no SAP is the highest (mean = 201µl/s) and is close to the theoretical value (205µl/s) from Poiseuille’s equation for viscous incompressible flow between smooth parallel plates. Except for synthetic seawater, the flow rate for other solutions decreases significantly with increasing SAP content, particularly beyond 0.4% vol. At 0.8% vol. SAP, the flow rate decreases by almost three orders of magnitude. Interestingly, for the SAP used in these tests (S1), the decrease in flow of tap-water, synthetic shallow groundwater and 0.12% NaCl is of the same order, consistent with the swelling ratio of S1 in these solutions being similar. In contrast, the swelling ratio of S1 in synthetic seawater is only 1/20 to 1/16 as large, thus crack sealing is not effective.

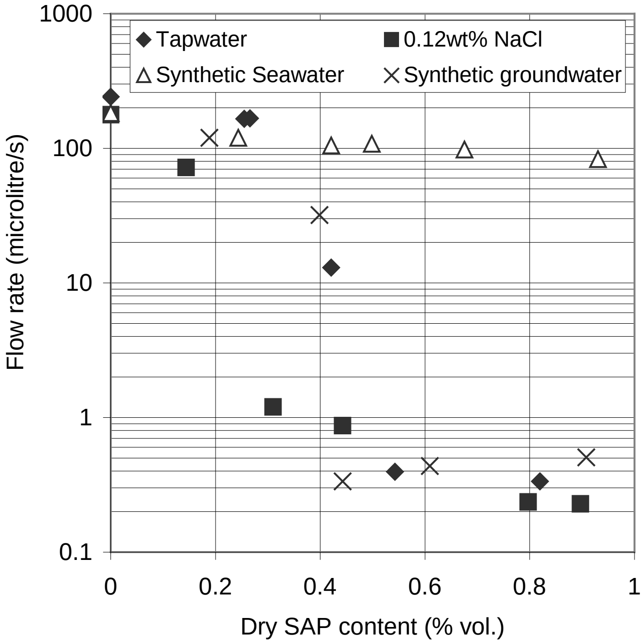


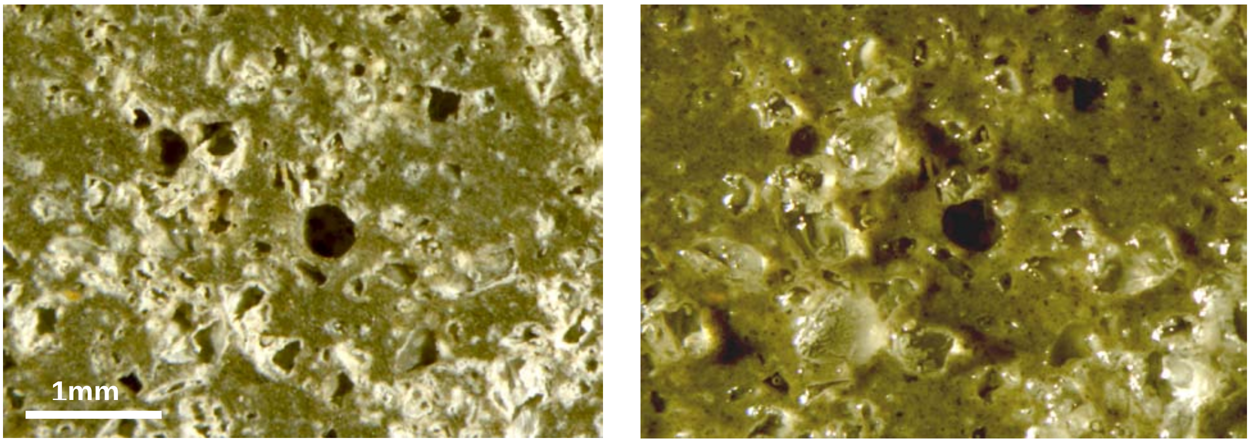
Fig. 4 Flow rates through a crack model containing different amounts of deposited SAP (S1) for various solutions

4.3 Microscopy

Fig. 5a shows the surface of a cement paste sample, which was ground to expose the SAP, observed under a stereomicroscope. Dry SAP particles lie inside the voids created by their initial swelling during mixing. When the surface is wetted with saturated lime solution, the SAP particles re-swell and expand beyond the original boundaries of the voids (Fig. 5b). This observation, although qualitative, demonstrates that SAP cast in cement paste has a significant amount of re-swelling capacity that may be exploited to block or reduce flow through cracks.

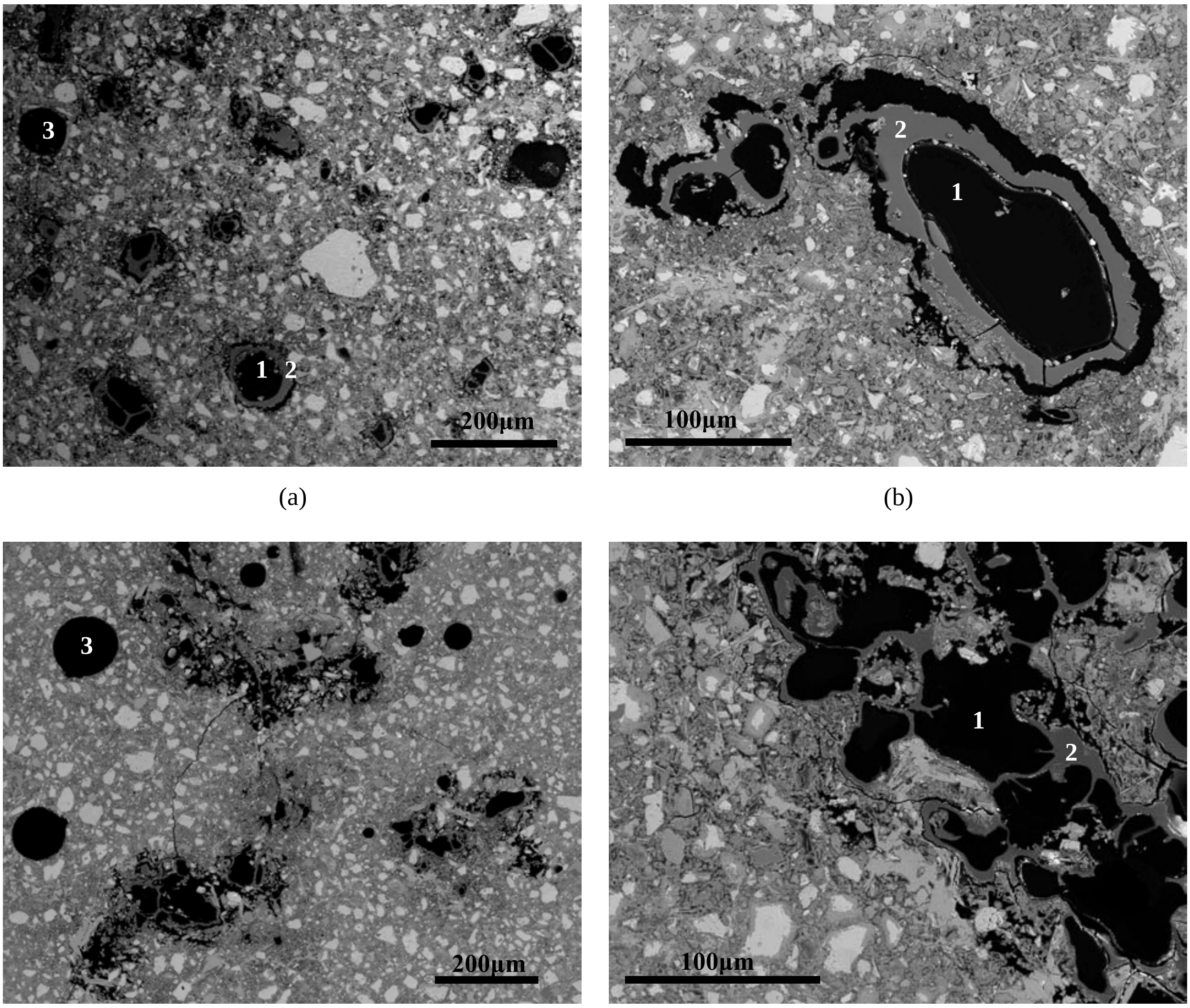
Fig. 6 shows BSE images of cement pastes containing 1% wt. of S1, S2 and S3, to highlight the size, shape and distribution of the SAP, and their effect on microstructure. The observed voids are either entrapped air or SAP voids. The entrapped air voids are spherical and do not contain the collapsed SAP, hence these can be differentiated from the SAP voids. The SAP voids are isolated and well distributed in the paste, and have sizes ranging from ~10µm to more than 500µm, depending on the initial size of the dry SAP and the amount of swelling in wet paste. Using image analysis, the volume fraction of the SAP voids and particles are estimated to be about 10% of the paste. Pastes containing S1 and S2 (Fig. 6a & b) display a gap between the paste and SAP due to shrinkage of the polymer. In paste containing S3 however, a good bond is retained (Fig. 6c & d) presumably because the higher specific surface of S3 (Fig. 2) allows better adhesion to the cement paste.

The presence of SAP clearly affects the paste microstructure, in particular, a cement content reduction near the SAP-paste interface due to particle packing effects (Fig. 6b & d). Preferential precipitation of calcium hydroxide in water-rich areas produces large portlandite deposits at the interface, while some microcracks connecting several SAP particles are also visible. These microstructural features resemble that of the paste-aggregate interface in typical concretes. However, the moisture released by SAP is expected to promote further hydration and microstructure development in the surrounding paste [9, 10].



(a) (b)

Fig. 5 Area matching stereo micrographs of a cement paste containing 1% wt. S5 at 0.5 w/c ratio, before and after wetting with tap-water



(a) (b)

(c) (d)

Fig.6 BSE images at various magnifications of 5-day old cement pastes at 0.36 w/c containing 1% wt. of: a) S1, b) S2, c & d) S3. The micrographs highlight the size, shape and distribution of the SAP voids (1), the collapsed SAP particle (2), entrapped air (3), and the microstructure at the SAP-cement paste interface.

5. Discussion

The SAPs used in this study are by no means the ideal ones for concrete. Since SAP can be produced with different physical and chemical properties that influence swelling behaviour, there is scope for optimisation. For efficient crack sealing in concrete, SAP should swell little when added to the mix so that its further swelling potential in a cracked situation is maximised. However, limiting initial swelling of SAP in the mix would reduce any benefits derived from internal curing.

Clearly, there are many issues that need to be examined before SAP can be used in concrete structures. The SAP introduces more voids in the cement paste that will inevitably affect the strength of the composite. It is well-known that an increase in air content of 1% in concrete translates into a decrease in compressive strength of around 5%[28]. Ideally SAP particles would be small and spherical, so that their disruption to the paste microstructure and effect on mechanical properties would be minimal. Related to the issue of SAP voids is their potential for frost protection, since they may accommodate the expansion of capillary water on freezing to avoid the development of disruptive pressure. This merits further investigation.

The actual swelling of SAP when cast in cement paste may be different from the free swelling value measured in a beaker of simulated pore solution. This is because real pore solution is more complex and variable, and the mixing and compaction during batching could further restrict SAP swelling. At later ages, the growth of hydration products may bond with the SAP, thereby affecting its ability to re-swell and seal cracks.

The flow through crack experiment is a simple demonstration of the potential of SAP to seal cracks under certain flow conditions. Testing crack models has the attraction over real samples that it allows better control of variables and aids in understanding. However, we do recognise that flow through a real crack in concrete is much more complicated and thus, research work in this area is on-going. We are also carrying out more detailed investigations to understand the swelling behaviour of SAP in cement paste, its response to various ions, in particular cations and its effect on hydration and microstructure. We are also developing models to predict crack sealing performance and to optimise mix design. Findings from these studies will be reported in the near future.

6. Conclusions

The potential of conventional SAP based on partially neutralised acrylate and acrylate/acrylamide copolymers as an admixture for self-sealing cracks in concrete was investigated. When added to concrete, the SAP swells by a relatively small amount due to the high alkalinity and ionic content of the pore solution. The water held in the SAP is available for cement hydration and as it is drawn out of the SAP, the SAP particles shrink. If the hardened concrete cracks in a wet environment, the subsequent ingress of an external solution with low ionic concentration may cause the exposed SAP to re-swell, blocking the crack and reducing flow. The swelling of the SAP in tap water and synthetic shallow groundwater was found to be much higher than that in synthetic pore solution. Transport testing found that the flow rate of tap-water, synthetic shallow groundwater and 0.12% NaCl through a 340μm wide model crack containing SAP is reduced substantially by using less than 1% vol. SAP. Qualitative observation using a stereomicroscope showed that SAP cast in cement paste has a significant amount of re-swelling capacity that may be exploited to block flow through cracks. The SAP introduces many voids that are isolated and distributed in the cement paste. Scanning electron microscopy in the backscattered mode showed other microstructural changes due to the presence of SAP including the modified distribution of cement particles, large portlandite deposits and some microcracking at the SAP-paste interface.

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