

An amphoteric hydrogel: Synthesis and application as an internal curing agent of concrete

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ABSTRACT: A new crosslinked amphoteric hydrogel (PAC) was synthesized and evaluated as an internal curing agent of concrete. PAC was prepared from acrylamide (AM) and 4-(2-((carboxylatomethyl)dimethylammonio)ethoxy)-4-oxobut-2-enoate (CMD) through free-radical polymerization by using ammonium persulfate (APS) as an initiator and methylene-bisacrylamide (MBA) as a crosslinker. The structure of the prepared polymer was verified by the IR spectra. The effects of the polymerization variables on the swelling capacity of PAC were investigated. The water absorbency of PAC was found to increase with increasing CMD/AM ratio, reach a maximum value, and decrease afterward. Increase of either APS or MBA content decreased the water absorbency. The highest water absorbency of PAC hydrogel (P7) achieved in deionized water, 0.1M NaCl solutions and 0.1M CaCl₂ solutions, was 306 g/g, 32 g/g, and 22 g/g, respectively. Compared with a commercial acrylate-based hydrogel 283HA, P7 was less sensitive to the existence of Ca²⁺ ions in cement pore solutions, and more effective in reducing the cracking tendency of cement pastes. Finally, mortars incorporated with proper amounts of P7 showed smaller drying shrinkage and higher compressive strength than that without hydrogel present. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42175.

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INTRODUCTION

Superabsorbent polymers or hydrogels are crosslinked hydrophilic networks that exhibit the ability of swelling, absorbing, and retaining a large amount of water within their structure. They have been applied in many area, including tissue engineering, biosensors, drug delivery systems, and agrochemistry.^{1–3} Another new and novel area of applications is in the construction industry; hydrogels are used as internal curing agents of concrete.^{4,5}

In concrete technology, curing is to maintain the moisture content in fresh concrete. That is important in developing the concrete microstructure and pore structure, and achieving the desired mechanical properties and durability. Traditional curing methods such as moist curing, membrane curing are considered as “external curing” ones. They can usually fulfill the curing purposes. However, inconvenience occurs in some practical applications. Therefore, the concept of “internal curing” or “self-curing” has been proposed and developed recently. Internal curing implies introduction to the concrete mixture a component, which serves as a curing agent. This agent can be either

inorganic materials such as lightweight aggregates or organic additives.^{4,5}

Water-soluble polymer and hydrogel are two types of organic internal curing agents. The former including polyvinyl alcohol can interact with water and decrease the water evaporation rate from concrete.^{6,7} In contrast, the latter can absorb and retain large amounts of water relative to its own weight. It acts as a water reservoir to release water gradually, supplement the water loss and increase the water retention or humidity of concrete compared to conventional concrete. As a result, addition of hydrogel could diminish or eliminate the shrinkage and cracking, and improve the durability of the cementitious materials. Especially for high performance concrete (HPC) made with low water/cement (w/c) ratios, autogenous shrinkage occurs due to self-desiccation. Hydrogels have proved capable of eliminating or considerably diminishing autogenous shrinkage so that the resulting HPC is less sensitive to cracking.^{8–12} Besides, hydrogels could also improve other properties such as self-sealing cracks,¹³ tensile creep,¹⁴ and thermal expansion of cementitious materials.¹⁵

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To date, most hydrogels used are cross-linked acrylate polymers (PAA) or acrylate-co-acrylamide copolymers (PAA/AM).^{8,9,12–14,16} For example, Schrofl *et al.*¹² studied the effects of the relative amount of anionic groups and the crosslinked density of PAA or PAA/AM hydrogel on the water absorption/desorption behavior in aqueous solutions, and on the compressive strength and autogenous shrinkage of the resulting mortars. Jensen and Hansen⁹ reported that autogenous shrinkage after setting and cracking during restrained hardening could be avoided when PAA/AM hydrogel was used in high performance concrete. Lee *et al.*¹³ reported that the crack is reduced substantially in cement pastes by using less than 1 vol % PAA/AM polymer.

Although some good results and valuable information have been obtained, there are still some aspects that could be further improved. It is known that cement contains four main components, i.e., dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), and tetracalcium aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$). When cement contacts water in concrete, it begins the hydration process and produces hydrated products. Meanwhile many ions including Na^+ , K^+ , Ca^{+2} , Fe^{+3} , Al^{+3} , OH^- , and SO_4^{-2} release to water and pore solutions are formed in cementitious materials.¹⁷ Therefore, to act as a good water reservoir, idea hydrogel should be able to absorb and retain a large amount of water not only in pure water but also in salt solutions. Although PAA or PAA/AM hydrogel could absorb more than 400 times its weight in deionized water, its water absorbency is much less in the presence of multivalent cationic ions such as Ca^{+2} , Fe^{+3} , Al^{+3} in the salt solutions or pore solutions.^{12,18}

In this study, an amphoteric hydrogel PAC as a concrete internal curing agent was prepared, as this type of polymer was reported to be salt-tolerant in saline solutions.^{19,20} The PAC was prepared from acrylamide (AM) and 4-(2-((carboxylatomethyl)dimethylammonio)ethoxy)-4-oxobut-2-enoate (CMD) under

basic conditions through free-radical polymerization. The structure of the prepared PAC was verified by the IR spectrum of the polymer. The water absorption behavior of this polymer in aqueous solutions was examined. The effects of monomer ratio, crosslinking agent and initiator content on the water absorbency of PAC were investigated. PAC samples were added in cementitious materials; their effects on the crack formation on the surface of cement pastes, and on the drying shrinkage and compressive strength of the resulting mortars were determined and discussed.

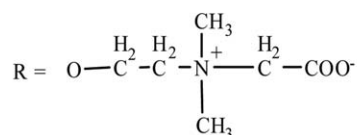
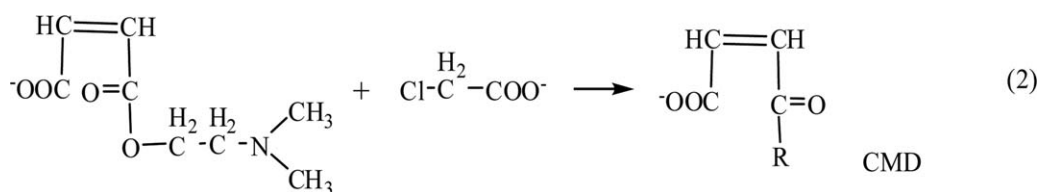
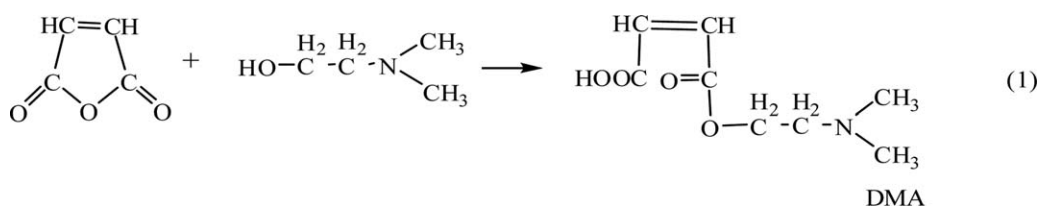
EXPERIMENTAL

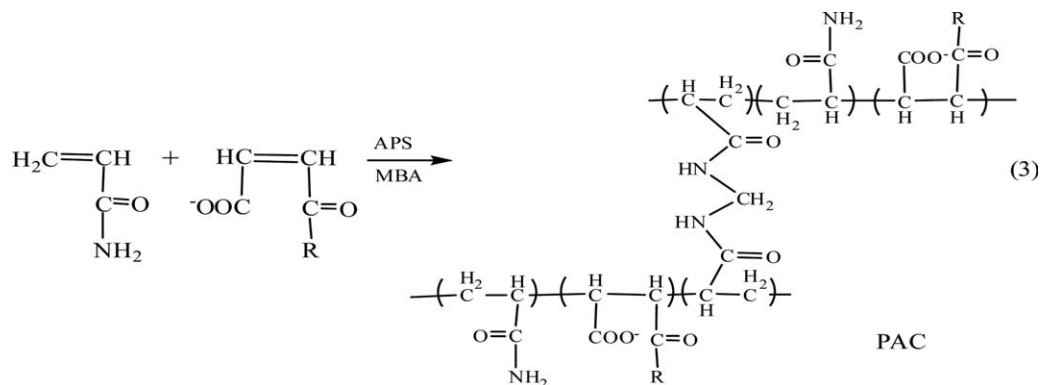
Materials

Acrylamide (AM, 98.5%), maleic anhydride (99%), *N,N*-dimethylethanolamine (99%), sodium chloroacetate (98%), ammonium persulfate (APS, 98%), and *N,N'*-methylenebisacrylamide (MBA, 99.5%) from Acros Organics (Morris Plains, NJ), were used without further purification. An amphoteric hydrogel PAC which contains both quaternary ammonium ($-\text{N}^+$) and carboxylate ($-\text{COO}^-$) groups in the polymeric structure was prepared. A commercial anionic polyacrylate hydrogel 283HA from Formosa Plastic Corporation (Taiwan) was also used for comparison. In addition, an acrylate-based superplasticizer A30 (SP) from SUN TECH (Taiwan) was used to adjust the fluidity of mortars. Unless specified otherwise, other chemicals used were all of analytical grade and all solutions were prepared using deionized water.

Preparation of PAC Hydrogel

PAC was prepared from AM and CMD using APS as an initiator and MBA as a crosslinker through a free radical polymerization. In turn, CMD was prepared from 3-((2-(dimethylamino)ethoxy)carbonyl)acrylic acid (DMA) and sodium chloroacetate. DMA was prepared from maleic anhydride and *N,N*-dimethylethanolamine.²¹ The reaction equations for preparing DMA, CMD, and PAC hydrogel are shown below:





An example of preparing DMA and CMD is as follows:²¹

Forty-nine grams of maleic anhydride was dissolved in 200 g of acetone, and then 44.6 g of *N,N*-dimethylethanolamine was added dropwise into a stirred reactor. The reaction proceeded for 6 h at 5°C. After the reaction, the mixture was vacuum filtered, washed with acetone, and the filtered solid powder was dried in a vacuum oven at room temperature for 24 h to collect DMA.

After obtaining the DMA, the formation of the monomer CMD was performed. That is, 74.8 g of DMA was dissolved in 300 mL of deionized water. The solution was adjusted to a pH of about 9–10, followed by addition of 46.6 g of sodium chloroacetate into a stirred reactor. Thereafter, the solution was mixed at 30°C for 24 h. Most of the solvent was then removed in a vacuum condenser, followed by washing with acetone. After the acetone was removed, the sample was dried in a vacuum oven at room temperature for 24 h to collect CMD.

After obtaining the CMD, PAC was synthesized. In this study, several PAC samples were prepared and tested. Table I shows the amounts of the chemicals used in preparing the samples. A

certain amount of AM and CMD were dissolved in 300 mL of distilled water in a stirred reactor. An aqueous solution containing APS and MBA was then added dropwise. The reactor was purged with N₂ gas, and the polymerization was carried out at 60°C for 1 h. At the end of the reaction, the gel was purified in methanol. The methanol was then removed to collect PAC. The hydrogel was immersed in an excess amount of deionized water for 2 days to remove the residual unreacted monomers. Swollen polymer was dried at 50°C for 24 h. Thereafter, the yield of the polymer prepared could be calculated. As listed in Table I, the yields of the prepared hydrogels ranged from 49.6% to 81%. In the following, all tested PAC samples were ground and had a particle size in the range of 16–20 mesh or 1.2–0.85 mm.

Identification of the Prepared PAC Hydrogel

The dried DMA, CMD, and PAC were ground into powder before structural determination. In identifying the chemical structure, we mixed proper amounts of the powder samples with predried KBr and pressed them into disks. Transmission IR spectra of the disks were recorded with a PerkinElmer Paragon 500 Fourier transform infrared spectrometer (Boston, MA).

Measurement of Water Absorbency of Hydrogel

The water absorption or swelling behavior of hydrogel was determined by a tea bag method reported elsewhere.²² A hydrogel sample of 0.05 g was put into a weighed tea bag and immersed in excess deionized water or salt solutions and allowed to soak for a certain time at room temperature. The swollen gel was taken out and allowed to drain so that excess liquid was removed from the tea bag. The bag was then weighed to determine the weight of the swollen gel. The water absorbency of the polymer was defined as the weight of absorbed water in the swollen sample which was put in aqueous solutions for a certain time divided by the weight of the dry sample. Water absorbency was expressed as grams of water per gram of sample (g/g).

Measurement of Water Retention of Hydrogel

The water retention behavior of hydrogel was also determined by the tea bag method. A hydrogel sample of 0.05 g was put into a weighed tea bag and immersed in excess deionized water at room temperature for 24 h to reach swelling equilibrium. Thereafter, the swollen sample was taken out and excess water separated from the bag. A water retention test was then carried out by putting the swollen sample in pore solutions obtained

Table I. Amounts of the Reactants Used in Preparing PAC Samples

Sample name	CMD (g)	AM (g)	APS (g)	MBA (g)	Yield (%)
P1	4.51	10	0.356	0.121	81.0
P2	10.5		0.404	0.136	78.3
P3	17.4		0.458	0.145	74.2
P4	27.0		0.534	0.182	71.5
P5	40.6		0.639	0.216	55.2
P6	61.0		0.799	0.270	49.6
P7	27.0	10.0	0.107	0.182	68.5
P8			0.213		^a
P9			0.267		-
P10			0.427		-
P11	27.0	10.0	0.107	0.218	-
P12				0.291	70.1
P13				0.364	-

^aNot measured.

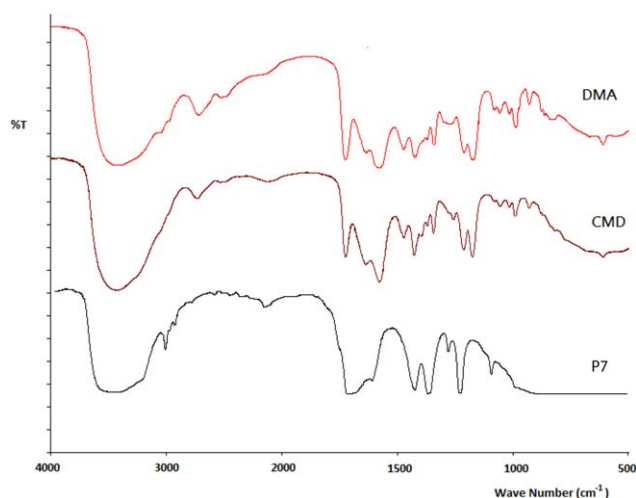


Figure 1. IR spectra of (1) DMA, (2) CMD and (3) P7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from cement pastes ($w/c = 0.3$). The water retention was defined as the weight of absorbed water in the swollen sample which was put in pore solutions for a certain time divided by the weight of the saturated absorbed water in the swollen sample initially. Water retention was expressed as percentage (%).

Preparation and Test of Cement Pastes and Mortars

Cement pastes were made by mixing water and type I Portland cement, with or without addition of hydrogel. The hydrogel was either PAC or 283HA. The water/cement ratio was 0.3; and the hydrogel/cement ratio ranged from 0 to 0.4 wt %.

The cracking tendency of cement pastes exposed to external drying immediately after casting was evaluated by modifying a Plastic Shrinkage Cracking Rig test method reported elsewhere.²³ The apparatus for this test consists primarily of a ring mold which contains two concentric steel rings with diameter 150 and 300 mm and depth 50 mm, having ribs attached to provide initiation of cracks in the paste sample. After casting, the ring paste samples were positioned under an air funnel. The opening between the paste surface and the funnel is 8 mm over the whole circumference of the outer ring. During testing, the wind velocity was 4.5 m/s, the air temperature was about 27°C, and relative humidity was 60% RH. After 1-day of blowing exposure, some cracks were occurred on the surface of ring samples and the crack index (Ci) of the sample was defined as the average accumulated crack width of all cracks on the surface of the samples as follows:

$$Ci = (\Sigma L1 + \Sigma L2) / 2 \quad (4)$$

where,

$\Sigma L1$: the crack widths in the heads of all cracks.

$\Sigma L2$: the crack widths in the tails of all cracks.

Mortars were made by the mixture of water, Type I Portland cement, standard Ottawa sand, and SP with or without addition of PAC hydrogel. Mixing of mortars was made following ASTM C305. The water/cement ratio was fixed at 0.485; the sand/cement ratio was fixed at 2.75; and the hydrogel/cement ratio

ranged from 0 to 0.4 wt %. Besides, proper amounts of SP were added so that the resulting mortars had required fluidity. The fluidity was indicated by the spread diameter of tested samples on a flow table after vibration according to ASTM C205. The tested mortars should reach required fluidity and have a spread diameter of 20.5–21.5 cm. Furthermore, the drying shrinkage of mortars was determined. The drying shrinkage was indicated by the length change of tested samples. Mortar specimens of $2.5 \times 2.5 \times 28.5 \text{ cm}^3$ were prepared, cured at 25°C and 60% RH, and the length change at the ages of 3–28 days was measured according to ASTM C157. Finally, the compressive strength of mortars was determined. Mortar specimens of $5 \times 5 \times 5 \text{ cm}^3$ were prepared, cured at 25°C and 60% RH, and the compressive strength at the ages of 3–28 days was measured according to ASTM C109.

RESULTS AND DISCUSSION

Structure of the Prepared PAC Hydrogel

The structures of typically prepared DMA, CMD, and PACs were verified from their IR spectra, as shown in Figure 1 and Supporting Information Figure S1. Figure 1(a) shows the IR spectrum of DMA, which displays an O–H stretching band at about 3418 cm^{-1} . The peak at 1724 cm^{-1} was due to the C=O stretching band of the carboxylate group. The peak at 1634 cm^{-1} represented the C=C stretching band. The peak at 1579 cm^{-1} represented the $-\text{COO}^-$ stretching band. The peak at 1211 cm^{-1} occurred because of C–N stretching. The peak at 1081 cm^{-1} represented the C–O stretching band. Figure 1(b) shows the IR spectrum of CMD, which displayed an O–H stretching band at about 3429 cm^{-1} , a C=O stretching band at 1723 cm^{-1} , a C=C stretching band at 1635 cm^{-1} , a $-\text{COO}^-$ stretching band at 1576 cm^{-1} , a C–N stretching band at 1213 cm^{-1} , and a C–O stretching band at 1077 cm^{-1} .

Figure 1(c) shows the IR spectrum of P7, which displayed an O–H stretching band overlapping with an N–H stretching band at about 3441 cm^{-1} , a C=O stretching band at 1713 cm^{-1} , a $-\text{COO}^-$ stretching band overlapping with an N–H bending band at 1603 cm^{-1} , a C–N stretching band at 1229 cm^{-1} , and a C–O stretching band at 1093 cm^{-1} . Compared to Figure 1(b), the IR spectrum in Figure 1(c) lacked the C=C absorption band and showed a sharper C=O stretching band at 1713 cm^{-1} , attributed to the polymerization of CMD and AM. Furthermore, the IR spectrum in Figure 1(c) showed a broader O–H stretching band overlapping with an N–H stretching band at about 3441 cm^{-1} , suggesting that P7 contained the primary amide group.^{24,25}

Water Absorption Behavior of PAC Hydrogel

To be used as an internal curing agent and act as a water reservoir, the hydrogel should present good water absorbency and swelling capability. In this study, PAC was prepared from AM and CMD through free-radical polymerization by using APS as an initiator and MBA as a crosslinker. It is clear that the reactant ratio, the crosslinker, and initiator content, are three main factors which affect the chemical structure of the hydrogel prepared and its swelling capability. In the following, the effects of these factors on the water absorption behavior of the resulting polymer were determined and discussed.

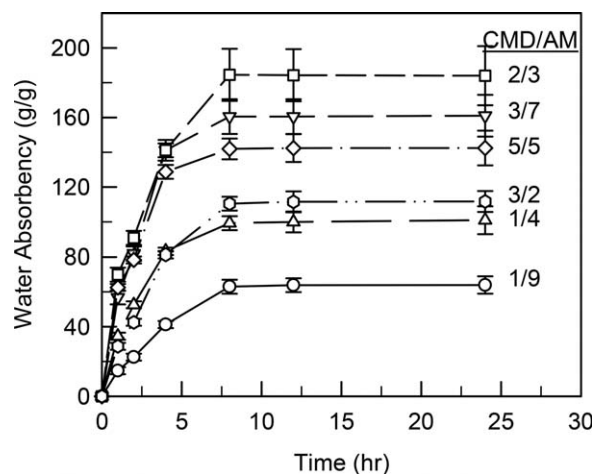


Figure 2. Water absorption behavior of PACs with different CMD/AM ratios in deionized water. (APS = 1.0%, MBA = 0.5%).

Figure 2 shows the water absorbency of PAC with different CMD/AM molar ratios in deionized water as a function of absorption time. All tested polymer samples were prepared using 1.0 mole % APS and 0.5 mole % MBA relative to monomer. A tea bag method was used to measure the amount of absorbed water by the polymer. Generally, the amount of absorbed water increased quickly with time in the beginning, and then approached a saturated and maximum value gradually. It took about 6 h to reach the saturated value. Furthermore, the effect of CMD/AM molar ratio on the saturated water absorbency (SWA) of PAC could be deduced from Figure 2. The SWA value was found to increase with increasing CMD/AM ratio when the molar ratio was less than 2/3. Clearly the ionic functional groups including quaternary ammonium ($-N^+$) and carboxylate ($-COO^-$) groups contained in the CMD moiety of the gel have higher affinity for water than the polar amide ($-CONH_2$) groups in the AM moiety.²⁶ Besides, more ionic groups in the gels cause more osmotic pressure difference. Therefore, the water absorbency of the hydrogel increased with increasing CMD content. When the CMD/AM ratio was greater than 2/3, the higher the CMD content, the lower was the SWA

value. It is noted that the positive quaternary ammonium groups would interact with the negative carboxylate groups inside the gel to form physical crosslinks. That results in the increase of effective crosslinks and decrease of water absorbency.^{27,28} Higher CMD content leads to more effective crosslinks and a lower SWA value.

Figure 3 shows the effect of APS content on the SWA value of PAC (CMD/AM = 2/3) in deionized water. The APS content ranged from 0.2 mole % to 1.0 mole %, and the MBA content was fixed at 0.5 mole % of monomer. It was observed that the SWA value decreased with increasing APS content. The maximum SWA value was of about 306 g/g which occurred at 0.2% of the initiator relative to monomer in mole. The reason is that more dosage of initiator generates more active free radicals, which would enhance the crosslinking density and generate tight network structure.²⁹ As a result, the water absorbency of PAC decreased with increasing initiator content.

Figure 4 shows the effect of MBA content on the SWA value of PAC (CMD/AM = 2/3) in deionized water. The APS content was fixed at 0.2 mole % and the MBA content ranged from 0.5 mole % to 1.0 mole % of monomer. When the added MBA to monomer molar ratio was equal to 0.5%, the hydrogel prepared showed the highest swelling capability and the saturated water absorbency was of about 306 g/g. As higher crosslinker content would result in higher crosslinking density, the resulting hydrogel showed lower swelling capability.^{30,31}

From the above results, PAC hydrogel with CMD/AM = 2/3 (P7) prepared using 0.2% APS and 0.5% MBA exhibited the highest water absorbency among all hydrogels prepared. In the following, the P7 sample was used and tested.

As mentioned earlier, pore solutions in cementitious materials contain many cations and anions including Na^+ , K^+ , Ca^{2+} , OH^- , SO_4^{2-} . Therefore, it is necessary to determine the swelling capacity of PAC in saline solutions. Figure 5 shows the water absorption of P7 in different aqueous solutions. The amount of absorbed water was found to increase with time, and then approach a saturated value. The water absorbency of P7 in

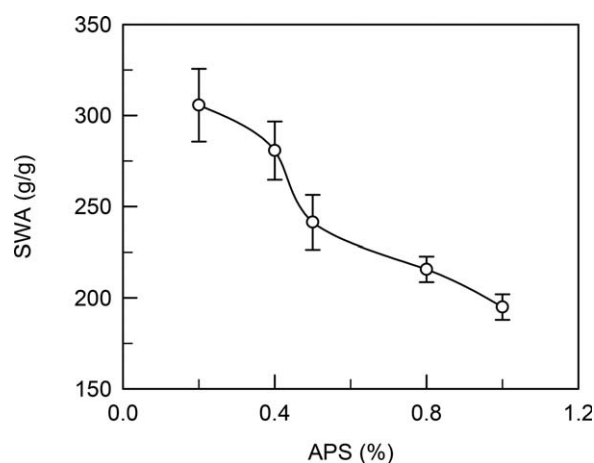


Figure 3. Effect of APS content on the SWA value of PAC in deionized water. (CMD/AM = 2/3, MBA = 0.5%).

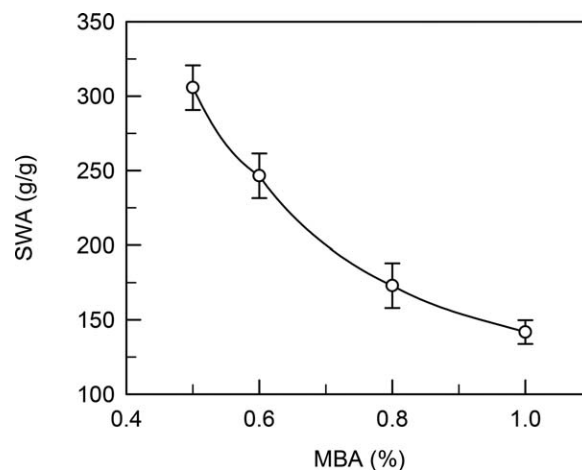


Figure 4. Effect of MBA content on the SWA value of PAC in deionized water. (CMD/AM = 2/3, APS = 0.2%).

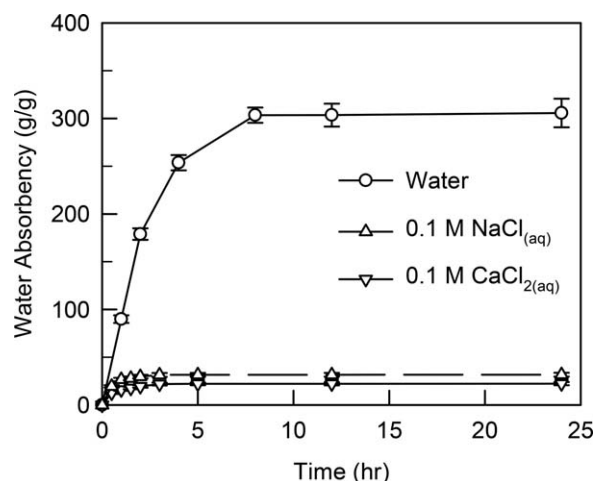


Figure 5. Water absorption behavior of P7 in salt solutions.

either 0.1M NaCl solutions or in 0.1M CaCl₂ solutions was clearly lower than that in deionized water. The absorption behavior of 283HA hydrogel in salt solutions was also examined and observed to be similar to that of P7. 283HA is a commercial crosslinked acrylate-based anionic polymer.

From the measurements, the SWA value of P7 in deionized water, 0.1M NaCl solutions and 0.1M CaCl₂ solutions, was 306 g/g, 32 g/g, and 22 g/g, respectively. The SWA value of 283HA in deionized water, 0.1M NaCl solutions and 0.1M CaCl₂ solutions, was 587 g/g, 70 g/g, and 7 g/g, respectively. Apparently, the added salts with greater cationic charges are more influential in declining the swelling property of 283HA than that of P7.

The swelling manner of anionic hydrogels in salt solutions is considered to be a polyelectrolyte behavior; the water absorbency decreases with increasing salt content or rising ionic strength in the external solution.^{27,28} The decrease in swelling capability is attributed to a charge screening effect of the cations from salts on the negative charge groups in the polymeric structure and a reduction of the osmotic pressure difference. Cations with higher charges cause more charge screen effects and also induce the formation of complexes with anionic groups that results in an increase in the crosslink density of the network. In contrast, the swelling manner of amphoteric hydrogels with a balanced stoichiometry (equal numbers of positive and negative charge groups) is reported to show an antipolyelectrolyte behavior; the water absorbency increases with increasing salt content or rising ionic strength. As mentioned earlier, the cationic groups would interact with the anionic groups inside the gel to form physical crosslinks. The added salts destabilize the physical crosslinks through charge-screening and reduce the effective crosslinking density. Therefore, the water absorbency increases with increasing salt content in solutions. As the number of anionic groups is greater than that of cationic groups in CMD, P7 is an anionic offset amphoteric gel; its swelling manner in salt solutions could be viewed as a combination of charge-balanced amphoteric and anionic hydrogel swelling behaviors. Therefore, P7 showed smaller swelling change in salt solutions and was more salt-tolerant than 283HA.

It is noted that although the swelling capability of P7 in deionized water or in NaCl solutions was less than that of 283HA, the water absorbency of the former hydrogel in CaCl₂ solutions was higher than that of the latter. Schröfl *et al.*¹² studied the relation between the molecular structure and the efficiency of hydrogel as concrete admixture. Their results indicated that hydrogel samples in cement pore solutions showed principal behavior very similar to that observed in the alkaline Ca²⁺ solution. Ca²⁺ has proved to be the most important ion in the pore solution with respect to the kinetics of liquid storage by the polymer. As the swelling behavior of PAC was less sensitive to the existence Ca²⁺ in aqueous solutions than the acrylate-based polymer, it suggests that the former would be a better candidate as a concrete internal curing agent.

Alternatively, the water retention test of P7 or 283HA soaked in pore solutions was carried out. First, the hydrogel sample was put in deionized water long enough to reach the saturated state. The swollen sample was then removed out and put in pore solutions of cement pastes ($w/c = 0.3$). Water was expected to release from the inside of polymer to pore solutions because of the osmotic pressure difference. Figure 6 shows the water retention (WR) of two hydrogels in cement pore solutions. The water retention is defined as the weight of absorbed water in the swollen sample which was soaked in pore solutions for a certain time divided by the weight of the saturated absorbed water in the swollen sample. In the beginning, the water retention of the swollen sample is 100%. When the swollen sample was soaked in pore solutions, the polymer would release water and the WR value decreased. For 283HA, the WR value was reduced to only 1.6% or about 9.4 g/g water remained inside the gel after soaking for 30 min. It indicated that 283HA released most of its absorbed water into pore solutions in a short time. In contrast, P7 shows a different water-releasing behavior. Along with soaking time, water was released initially from the polymer, and then re-absorbed afterwards. The transition from water release to water re-absorption was due to a conversion of amide groups to carboxylate groups in the polymeric structure under basic conditions.³² The minimum water retention of P7 at the transition point was 32% or 98 g/g. The

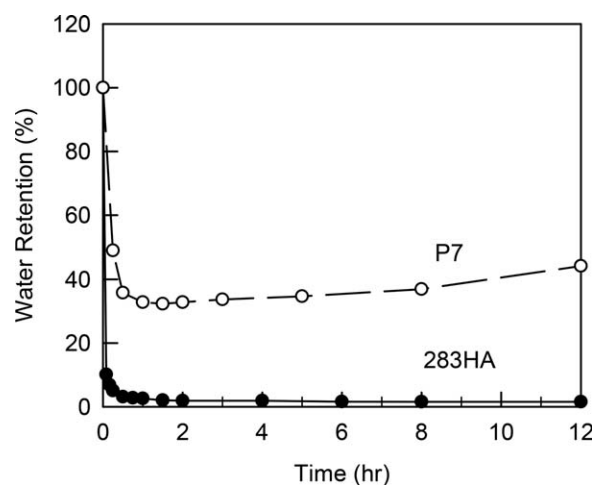


Figure 6. Water retention of 283HA and P7 in deionized water.



Figure 7. Crack tendency of cement pastes with (a) 0%, (b) 0.1%, and (c) 0.4% 283HA after 1-day air blowing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

time required to reach the transition state is of about 1.5 h. Compared to 283HA, the water-releasing rate of P7 was slower and the minimum WR value was 10 times higher, indicating that this amphoteric polymer could retain more water and act as a better water reservoir in concrete.

Properties of Hardened Cementitious Materials with P7 Hydrogel

Plastic shrinkage cracks occur when the evaporation of moisture at the surface of the cement pastes is greater than the availability of rising bleed water to replenish the surface moisture. In this study, a modified Plastic Shrinkage Cracking Rig test was used to evaluate the cracking tendency of cement pastes exposed to external drying immediately after casting.²³ Figure 7 shows the crack tendency of cement pastes with 283HA after 1-day air blowing. Several cracks were found on the surface of cement pastes without hydrogel present; the crack index (Ci) was 0.53 mm. The Ci value of cement pastes with 0.1 wt % 283HA was 0.36 mm. When cement pastes contained 0.4 wt % polymer, fewer and smaller cracks were observed and the Ci value was 0.09 mm. These results confirm that hydrogel could release water, retain the moisture in cement pastes, and reduce the plastic shrinkage and cracks. The more the hydrogel was incorporated, the fewer and smaller cracks occurred on the surface of the pastes. Figure 8 shows the crack tendency of cement pastes with P7 after 1-day air blowing. The Ci value was reduced from 0.53 mm to 0.22 mm when 0.1% P7 was added. When cement

pastes contained 0.2 wt % polymer or more, almost no cracks occurred and the Ci value was close to 0 mm. These results indicated that the required amount of P7 was lower than that of 283HA to minimize the crack occurrence on the surface of the pastes. Clearly, the prepared amphoteric polymer is more effective than 283HA in reducing the plastic shrinkage of cement pastes.

After hardening, concrete or mortars begin to shrink as water not consumed by cement hydration leaves the cementitious materials and drying shrinkage occurs. Figure 9 shows the effect of P7 content on the drying shrinkage or length change of mortars cured at different ages. Generally, the length change was increased with curing age. Furthermore, the drying shrinkage of mortars was found to increase with increasing hydrogel dosage when the polymer content was less than 0.2 wt %. There are two factors needed to be considered. First, incorporation of hydrogel in mortars would increase the moisture and reduce the length change. Second, the density of hydrogel is less than that of cement or sand particles. The added polymer in mortars tended to move up and aggregated each other. The aggregation would make the released water from hydrogel be poorly distributed in mortars, which was not beneficial to diminish the drying shrinkage. The aggregated phenomenon became worse when more hydrogel was incorporated. For mortars incorporated with 0.2 wt % P7 or less, the first factor appeared to be more influential. In contrast, the second factor became dominant when

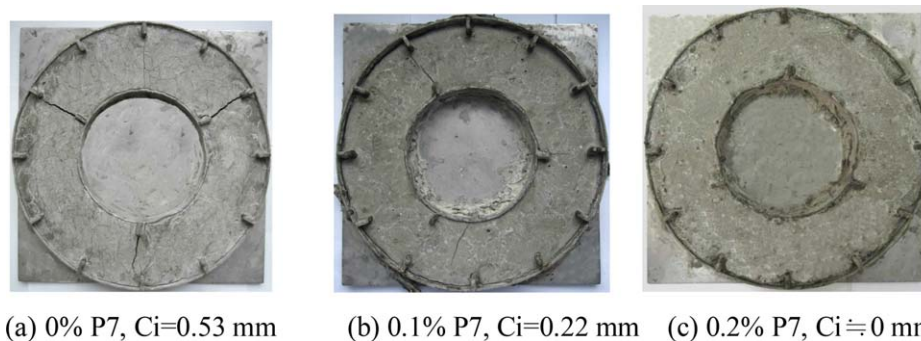


Figure 8. Crack tendency of cement pastes with (a) 0%, (b) 0.1%, and (c) 0.2% P7 after 1-day air blowing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

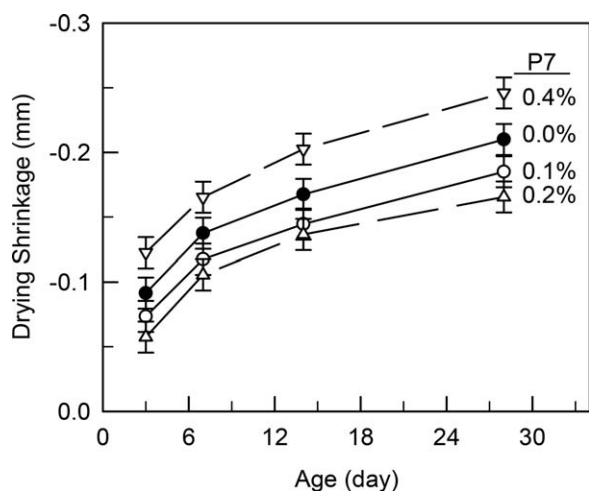


Figure 9. Drying shrinkage of mortars with P7 at 3–28 days.

mortars contained higher amount of polymer. Apparently, mortars with 0.2 wt % P7 showed the smallest drying shrinkage. The 28-day length change of the reference mortar without hydrogel present was -0.20 mm. The 28-day drying shrinkage value of mortars with 0.2 wt % hydrogel was -0.15 mm, or a reduction of length change by 25% from the reference.

Figure 10 shows the effect of P7 content on the compressive strength of mortars cured at different ages. As expected, the strength increased with curing time initially, and became leveling-off gradually. Depending on the hydrogel content, the strength of mortars with hydrogel could be greater or lower than that of the reference one without polymer incorporated. Mortars incorporated with 0.2 wt % P7 or less showed higher compressive strength than the reference one. There are several factors needed to be considered.³³ First, incorporation of hydrogel in mortars would increase the moisture and the degree of the cement hydration; this promoted the strength development. Second, hydrogel became swollen when it absorbed water; the more water the polymer absorbed, the more swelling the hydrogel became. Hydrogel was much weaker compared with cement or sand particles. The polymer became a weak point inside the

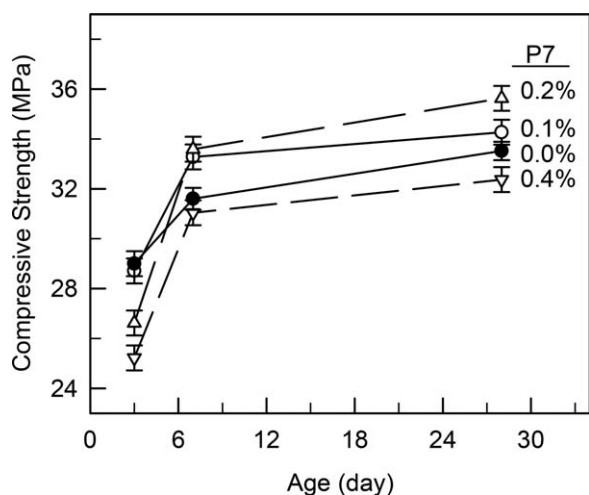


Figure 10. Compressive strength of mortars with P7 at 3–28 days.

mortar matrix. Third, when water was released from swollen hydrogel to maintain the moisture in mortars, the polymer would shrink and leave pores around the gel structure, which also decreased the strength of mortars. The tested result indicated that the first factor was dominant over the other two when the added PAC content was up to 0.2 wt %. The 28-day strength value of mortars with 0.2 wt % P7 was 35.6 MPa, which is 12% greater than that of the reference (33.5 MPa).

CONCLUSIONS

A new crosslinked amphoteric hydrogel (PAC) was synthesized from AM and CMD through free-radical polymerization by using APS as an initiator and MBA as a crosslinker. The water absorbency of PAC was found to increase with increasing CMD/AM ratio initially, reach a maximum value, and decrease afterward. Increase of either APS or MBA content decreased the water absorbency. P7 with CMD/AM = 2/3 prepared by addition of 0.2% APS and 0.5% MBA showed the highest swelling capability (306 g/g). Compared with a commercial acrylate-based hydrogel 283HA, P7 is more salt-tolerant and less sensitive to the existence Ca^{2+} in cement pore solutions, and more effective in reducing earlier crack occurrence of cement pastes. Addition of proper amounts of this polymer could reduce the drying shrinkage and compressive strength of the resulting mortars. Consequently, P7 has proved to be a potential internal curing agent of concrete.

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