

Application of cross-linked poly(acrylic acid)-poly(styrene-*alt*-maleic anhydride) core-shell microcapsule absorbents in cement mortars

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Abstract—We synthesized core-shell microcapsule absorbents with crosslinked poly(acrylic acid) (PAA) as the core and poly(styrene-*alt*-maleic anhydride) (cPAA-PSMA) as the shell by the precipitation polymerization method for delayed absorption of excess water in cement mortar. To control the shell thickness, cPAA-PSMA capsules were synthesized with the core-to-shell monomer mass ratios of 1 : 0 (cPAA #1), 1 : 0.5 (cPAA-PSMA #2), 1 : 1 (cPAA-PSMA #3), and 1 : 1.5 (cPAA-PSMA #4). The viscosity of the cement paste with cPAA-PSMA #4 absorbent increased slowly until 90 minutes after absorbent addition, beyond which it increased rapidly. This suggests that mortars with cPAA-PSMA #4 absorbents can secure up to 90 minutes of working time. Incorporation of 1.0 wt% cPAA-PSMA #4 into cement mortar increased the compressive and flexural strengths by approximately 35% and 22%, respectively, compared to those of cement mortars without absorbents.

Keywords: cPAA-PSMA, Microcapsule, Absorbent, E. Mortar, C. Compressive Strength

INTRODUCTION

It is common to add more water than is theoretically necessary when making concrete. The theoretical water/cement (W/C) ratio is known to be 0.25-0.30, but generally, a W/C ratio of 0.50-0.60 is adopted when making concrete. The purpose of this excess 25-30 wt% water is to enhance the workability of concrete [1,2]; however, this excess water can cause a decrease in compressive strength, bleeding, and an increase in shrinkage cracks in the concrete [2,3]. It also decreases the long-term durability of concrete through enabling chloride ion permeation, causing carbonation, and increasing the severity of the adverse effects of freeze-thaw cycles [4].

Several studies have focused on preventing the problems associated with the addition of excess water [2,5,6]. One such research employed the dewatering mold form (DMF), which has many holes on its surface to drain excessive water from the concrete [5]. However, this method drains only the excess water from the body of the concrete; the excess water at the top is drained out effectively, though, owing to the small self-weight pressure. Another such research used a water-reducing agent, a surfactant, to reduce the excess water added to the cement, and thereby reduce the viscosity of the cement paste [6]. However, the properties of concrete or mortar can be adversely affected by the uncontrolled temperature increment caused by the hydration reaction that occurs in the cement paste upon using the water-reducing agent [7]. Other studies focused on addressing the excess water problem used water absorbing materials such as poly(vinyl alcohol) [8] or poly(sodium acrylate) [2].

The drawback of using such a material is that after the initial absorption of water by it, the hydration reaction in the cement is hindered and the viscosity of the cement increases rapidly as a result, thus reducing the workability of concrete.

Therefore, we investigated the synthesis of core-shell structured microcapsule absorbents that do not absorb water immediately after the concrete mixing has started, but do so after a specific time delay, after which the shell parts of the absorbents start to dissolve in the alkaline cement water while the core parts start to absorb water. In this study, we characterized the application of synthesized core and core-shell structure microcapsule absorbents for only the cements that were assessed in our previous work [9]. The characteristics of the cement paste with the core and the core-shell structure absorbents that were evaluated in this study include the changes in viscosity and slump flow. After manufacturing the mortars, we measured their compressive and flexural strengths, and analyzed the fractured surfaces of the cracked mortars cured for 28 days by field emission scanning electron microscopy (FE-SEM).

EXPERIMENTAL

1. Materials and Apparatus

We performed precipitation polymerization to make microcapsule absorbents with crosslinked poly(acrylic acid) (PAA) as the core and poly(styrene-*alt*-maleic anhydride) (PSMA) as the shell (PAA-PSMA). Toluene (OCI Company Ltd.) was used as a solvent. Acrylic acid (AA, Ducksan Pure Chemical) was passed through the inhibitor-remover column (Aldrich) before use. The cross-linking agent *N,N'*-methylene bisacrylamide (MBA, Acros Organic, 96%), styrene (St, Aldrich), maleic anhydride (MA, Aldrich), 2,2'-azobisisobutyronitrile (AIBN, Daejung) were all used without any further purifi-

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Table 1. Chemical composition of ordinary Portland cement

Composition	wt%
SiO ₂	21.480
Al ₂ O ₃	5.290
Fe ₂ O ₃	3.030
CaO	63.310
MgO	2.800
SO ₃	2.450
Na ₂ O	0.072
K ₂ O	0.873
Alkali	0.800
Ignition loss	1.160

cation. Ordinary Portland cement (ASTM type I, Ssangyong cement, called "cement") was used as received. Table 1 lists the chemical composition of the Portland cement used in this study. The chemical composition of Portland cement shown in Table 1 can form alkaline aqueous solution in water. This formed alkaline aqueous solution can dissolve the shell part of synthesized microcapsule absorbents. The polymerization apparatus used in this research was a Pyrex glass reaction flask (500 mL) with a five neck cover. Stirrer (WiseStir™, Daihan Scientific Co.) and water bath (WB-23, SIBATA) were also used.

2. Preparation Polymerization

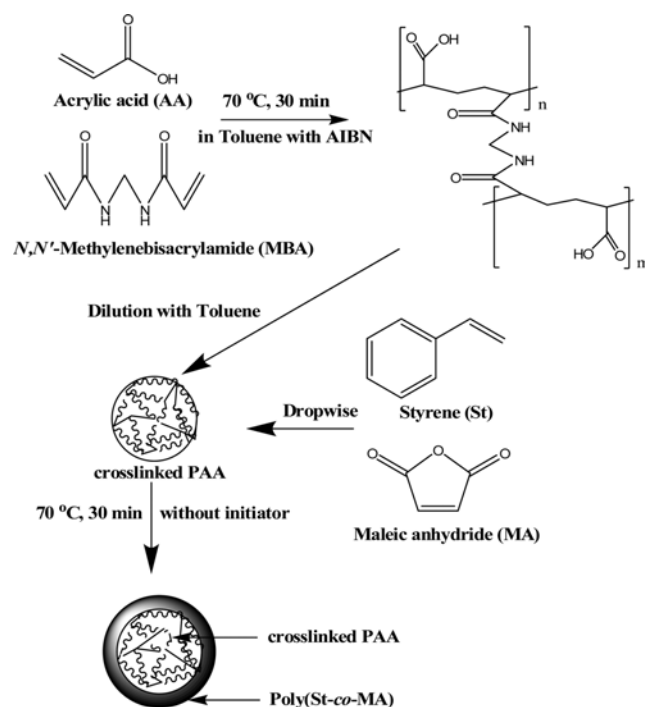
Polymerization of core and core-shell structure absorbents was performed as reported in our previous work [9]. In brief, 100 mL toluene and 0.6 g AIBN were placed in the 500 mL glass reactor, which was then covered for the polymerization to occur. The temperature was increased to and then maintained at 70 °C using a water bath. The reactor was purged with N₂ gas, and continuously stirred at 100 rpm to dissolve the AIBN in toluene. A total of 30 g of AA and 0.1 g of MBA were mixed in a 100 mL beaker; this solution was then poured through a dropping funnel into the reactor dropwise in 30 minutes. The reaction mixture in the reactor polymerized further for an additional 30 minutes [4,5]. The polymerized products were filtered through a filter paper, dried at 50 °C in a drying oven to remove excess toluene, and finally dried in a vacuum oven for 24 hours. The resulting dried solid was termed cPAA #1 (core to shell monomer mass ratios of 1 : 0).

The shell of the cPAA-PSMA core-shell microcapsule absorbent was synthesized by using different masses of St and MA monomers to vary the thickness of the shell in relation to the size of the core cPAA #1 (St and MA make an almost perfectly alternating copolymer, and therefore, their molar ratio for reaction is always 1 : 1). Shell polymerization was performed according to [10]. After dissolving MA and St in toluene, we added this solution dropwise to the cPAA #1 mixture through a dropping funnel over 30 min, after which the resulting solution was polymerized for an additional hour under the same condition (at 70 °C, no additional initiator) used for the synthesis of the core polymer. The compositions employed are shown in Table 2.

Upon completion of the shell polymerization, the reactor was cooled to room temperature by exchanging the hot water with tap water at room temperature tap water in a water bath. The polym-

Table 2. Compositions used for cPAA-PSMA polymerization

Core	Polymer	AA (g)	MBA (g)	Toluene (mL)
	cPAA #1		30.00	0.10
Shell	Polymer	MA (g)	Styrene (g)	Toluene (mL)
	cPAA-PSMA #2	7.35	8.10	100
	cPAA-PSMA #3	14.70	16.20	200
	cPAA-PSMA #4	22.05	24.30	300



Scheme 1. Scheme of polymerization of microcapsule absorbent with water absorbent core-alkali soluble shell parts for cement paste.

erized product in the reactor was then filtered through filter paper, washed three times with toluene, dried at 50 °C in an oven to remove excess toluene, and further dried in a vacuum oven for 24 h. All preparation process of microcapsule absorbent polymerization is shown in Scheme 1.

3. Characterization

3-1. Measurement of Cement Paste Viscosity

After preparation of cement pastes with a W/C ratio of 1 : 2, changes in the viscosity of the cement paste with microcapsule absorbents of cPAA-PSMA content, in this case 0.25 wt% considering only the weight of the core of the core-shell structure, were measured for 4 hours. The reason for fixing the mixing ratio of cPAA-PSMA as 0.25 wt% considering only the weight of the core of the core-shell structure was to absorb any excess water beyond the theoretically necessary amount. Viscosity changes with time were measured by rotating an "s5 spindle" at 6 rpm using a viscometer (Brookfield viscometer DV II + programmable).

3-2. Slump Flow Test

To measure the shell dissolution rate of microcapsule absorbents

in mortar, the mortar was first made according to KS L ISO 679, and the slump flow with time was measured by KS L 5105 for a total duration of 3 hours with measurements being recorded every 30 minutes. After the flowing plate was dropped 25 times from a height of 127 mm, the diameters of the now spread mortar were measured at four different positions. These four time measurements were averaged and expressed as percentage increase compared to corresponding averaged value for the mortar without any microcapsule absorbent.

3-3. Measurement of Mortar Compressive and Flexural Strengths

Mortars for compressive and flexural strength measurements were made and measured according to KS L ISO 679. Cement mortar without absorbents (Plain) was set as a control and compared with mortars with polymerized absorbents. Compressive strength, R_c (N/mm²), was calculated as in Eq. (1) by dividing the maximum load (F_c) by the cross sectional area (A) of the specimen.

$$R_c = F_c / A \quad (1)$$

In this equation, F_c is the maximum compressive cracking load (N) and A is the area of pressurization plate.

Flexural strength, R_f (N/mm²), was calculated by Eq. (2) under a loading rate of 50 N/s.

$$R_f = \frac{1.5F_f l}{b^3} \quad (2)$$

In this equation, F_f is the axial load (N) at the fracture central point of specimen, l is the length (mm) between supporters, and b is the length (mm) of side that is at a right angle to the fractured side.

Compressive and flexural strength measurements were conducted for specimens that were cured for 3 days, 7 days, and 28 days. The measurement results were averaged from three individual measurements for each.

3-4. FE-SEM Analysis of Cracked Mortars After 28 Days

After the compressive strength testing of the mortars, the crack surface of each mortar specimen was analyzed by FE-SEM (Hitachi S-4300) after sputtering a thin layer of Pt on it to improve conductivity.

3-5. Porosimetry Analysis of Cracked 28 Day-cured Mortars

The porosity and pore size distribution of cracked mortars from the compressive strength testing were analyzed using a porosimeter (Micromeritics Instrument Corporation AutoPore IV9500) according to ISO 15901.

RESULTS AND DISCUSSION

1. Viscosity of Cement Paste with cPAA-PSMA

To measure the change in viscosity corresponding to the time after addition of absorbent, we made cPAA #1 and cPAA-PSMA-added cement pastes with the core part cPAA being 0.25 wt% of the total cement paste weight (Table 3), assuming the swelling ratio of cPAA to be 100, to absorb excess water. Additionally, we fixed the W/C ratio as 1 : 2 (50 parts: 100 parts). The swelling ratio value of 100 was determined in our previous study on cPAA, which showed a swelling ratio of 110 [9] after 1,440 min of the swelling experiment. The change of paste viscosity with time was measured from

Table 3. Mixture compositions for the viscosity measurement of cement pastes with cPAA and cPAA-PSMA

Polymer	Added amount (g)	Cement (g)	Water (g)
cPAA #1	0.75		
cPAA-PSMA #2	1.13	300	150
cPAA-PSMA #3	1.50		
cPAA-PSMA #4	1.90		

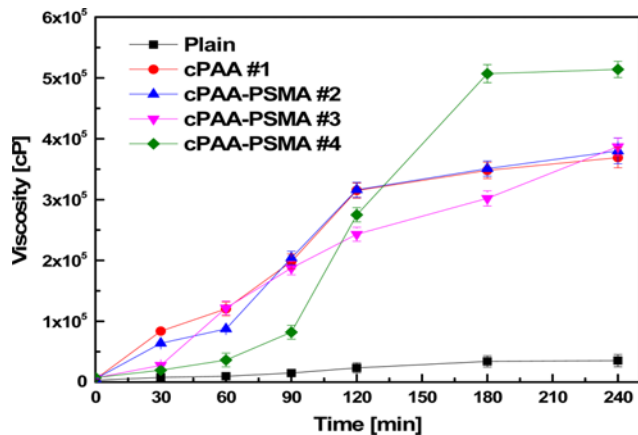


Fig. 1. Viscosities of cement pastes with cPAA-PSMA series.

0 to 4 h in this study, and the results are shown in Fig. 1.

As shown in Fig. 1, it is evident that the viscosity increases slowly with time for the plain samples. However, the viscosity of the cement pastes with cPAA #1 increases more rapidly compared to the plain sample. The change in viscosity with time of the cement pastes with cPAA-PSMA #2 (core to shell monomer mass ratios of 1 : 0.5) shows almost the same trend as that of the cPAA #1-added cement pastes, possibly due to incomplete or very thin shell formation in cPAA-PSMA #2 [9]. However, the viscosities of the cement pastes with cPAA-PSMA #3 (core to shell monomer mass ratios of 1 : 1) and cPAA-PSMA #4 (core to shell monomer mass ratios of 1 : 1.5) increase slowly for 30 minutes and 90 minutes after their addition, respectively, beyond which, they increase rapidly. This is caused by the hydrolysis and dissolution of the shell part of the cPAA-PSMA core-shell structures in cement saturated aqueous solution (CSAS), and the absorption of excess water by the neutralized cPAA core part [9]. In light of this, given that cPAA-PSMA #4 has a thicker shell than cPAA-PSMA #3, the cPAA-PSMA #4-added cement pastes showed more delayed viscosity than did the cPAA-PSMA #3-added cement pastes. From these results, it is clear that by using cPAA-PSMA #3 and cPAA-PSMA #4 microcapsule absorbents, we can secure at least 30 minutes and 90 minutes of working time, respectively, for the cement paste.

2. Slump Flow with Time

To investigate the dissolution rate of the shell and the formation of the core-shell structure of microcapsule absorbents, plain mortar and mortars with 1.0 wt% of cPAA-PSMA #2, cPAA-PSMA #3, and cPAA-PSMA #4 on the core weight basis of total cement weight were made. The W/C was set as 0.65, and the cement to sand ratio as 1 : 3 according to KS L 5105. We measured the mortar flow as a

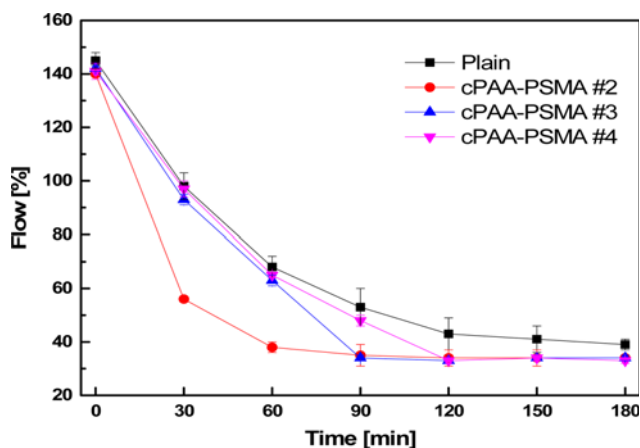


Fig. 2. Slump flows of cement mortars using the cPAA-PSMA series as a function of time.

function of time, making a measurement every 30 minutes for a total test duration of 3 h. The results are shown in Fig. 2. As shown, the slump flow for the plain sample was 98% at 30 minutes and 43% at 120 minutes. Note that after 120 minutes, only a small decrease in slump flow was observed, from 43% to 39%. However, for the 1.0 wt% cPAA-PSMA #2-added mortar, we found a rapid decrease of slump flow, 56% at 30 minutes and 38% at 60 minutes, due to either incomplete or very thin shell formation [9]. Incomplete shell formation could be attributed to the presence of lower water content left after the absorption of excess water [11,12].

Mortars with 1.0 wt% cPAA-PSMA #3 and cPAA-PSMA #4 showed similar slump flow decrease trends as that for plain mortar for 60 min and 90 min after their addition, respectively. These results support the observation that complete dissolution of the shell part occurs in the case of cPAA-PSMA #3 and cPAA-PSMA #4, and the absorption of excess water in mortar by the core part occurring concurrently with shell dissolution. Based on these slump flow test results, the addition of cPAA-PSMA #3 or cPAA-PSMA #4 absorbents to mortars can help secure 60 or 90 minutes of working time; these are good results that correspond well to the respective viscosity changes for these materials.

3. Measurement of Mortar Compressive and Flexural Strengths

Generally, the strength of mortar with carboxylic polymer has increased, which is caused by interaction of calcium hydroxide with carboxylic acid groups of the polymer. On the basis of this theory, the effect of cPAA-PSMA addition on the compressive and flexural strengths of mortar was investigated. Experiments were conducted to understand the influence of the dissolution of the shell part of the microcapsule absorbents into CSAS after some delay and the absorption of excess water by the core part on the strength attributes. To determine the optimum amount of cPAA-PSMA addition, we added 0.5, 1.0, and 1.5 wt% of cPAA-PSMA #3, based on the core weight basis, to the cement paste made with a W/C ratio of 0.50 and cement to sand ratio of 1:3. Next, the compressive strengths of the mortars were evaluated using specimens specifically made for the tests. The results are shown in Table 4.

As shown in Table 4, the compressive strength of the mortar with 1.0 wt% cPAA-PSMA #3, on the core weight basis, after 28

Table 4. Compressive strengths of cement mortars with various amount of cPAA-PSMA #3

Series	Core amount (%)	Compressive strength (MPa) (σ^a)		
		3 Days	7 Days	28 Days
Plain	0	26.2(\pm 0.3)	31.7(\pm 0.5)	32.3(\pm 0.4)
	0.5	28.7(\pm 0.1)	37.6(\pm 0.3)	39.8(\pm 0.3)
cPAA-PSMA #3	1.0	30.2(\pm 0.2)	39.1(\pm 0.5)	42.3(\pm 0.2)
	1.5	25.6(\pm 0.2)	30.7(\pm 0.4)	32.0(\pm 0.3)

^a σ = Standard deviation

days of curing, shows the highest value of 42.3 MPa. However, mortars with 0.5 wt% and 1.5 wt% show relatively lower values of 39.8 MPa and 32.0 MPa, respectively. By comparing these results with the compressive strength of the plain sample, it is clear that a 30% increase is obtained for 1 wt% cPAA-PSMA #3-added specimens, and a 15% increase is obtained for 0.5 wt% cPAA-PSMA #3-added specimens. Almost no increase was found, however, for the 1.5 wt% cPAA-PSMA #3-added specimens. This is because any mortar needs water for the hydration reaction to occur during curing to form the C-S-H crystals [13,14]. However, an excess amount of cPAA-PSMA may retard the hydration reaction by absorbing the excess water in mortar and cause excess swelling of the microcapsule absorbents, thereby decreasing the compressive strength of the mortar [2,15]. To form C-S-H crystals, it is necessary to have an optimum amount of water (0.25-0.30 W/C ratio) in cement paste.

The technique employed for the evaluation of the compressive strength for cPAA-PSMA #3-added specimens, the same mentioned in a previous study, was employed to evaluate the compressive and flexural strengths of mortars with 1.0 wt% of cPAA #1, cPAA-PSMA #2, and cPAA-PSMA #4 [16]. Figs. 3 and 4 show the compressive and flexural strengths, respectively, of cement mortars with the different cPAA-PSMA contents. As shown in Fig. 3, the compressive strengths of mortars with cPAA #1 are 21.1, 24.3, and 25.9 MPa after 3, 7, and 28 days of curing, respectively. These values are lower than those of the plain samples, which had compressive strengths

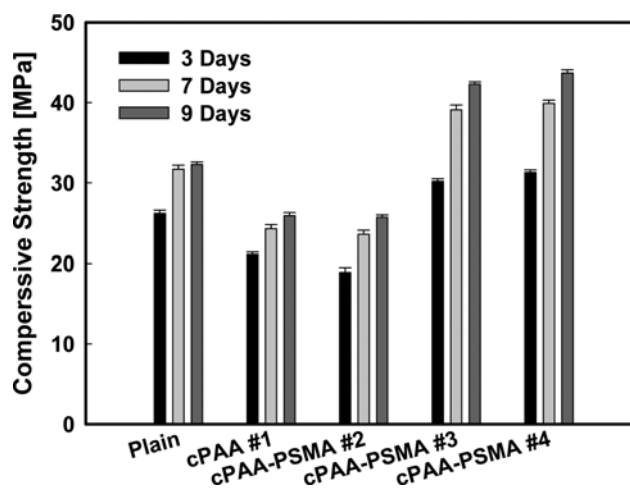


Fig. 3. Compressive strengths of cement mortars with cPAA-PSMA series.

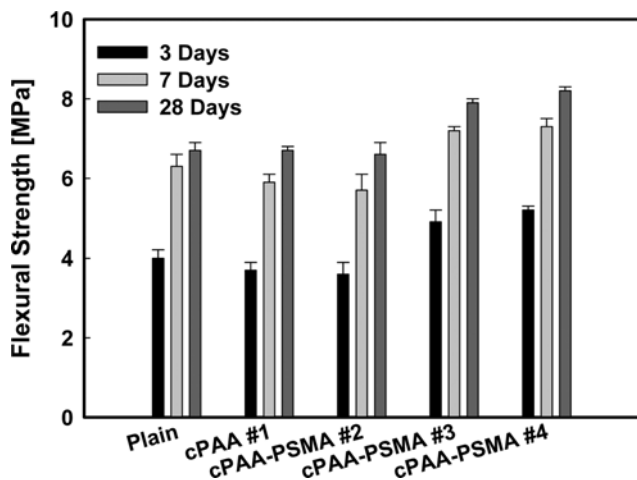


Fig. 4. Flexural strengths of cement mortars with cPAA-PSMA series.

of 26.2, 31.7 and 32.3 MPa for 3, 7, and 28 days of curing, respectively. This decrease in compressive strength may have been caused by insufficient occurrence of the hydration reaction in the mortar due to the water necessary for the hydration reaction being absorbed by cPAA #1. On the other hand, the compressive strengths of mortars with cPAA-PSMA #2 are 18.9, 23.6, and 25.7 MPa for 3, 7, and 28 days of curing, respectively. These values are similar to, or even a little lower than, those of mortars with cPAA #1. This decrease may be attributed to the excessive absorption of water during the preparation of the mortar with the cPAA-PSMA #2 absorbent, which has either a very thin shell or an incompletely formed shell owing to the small amount of shell monomer added during polymerization. For 3, 7, and 28 days of curing, the compressive strengths of mortars with cPAA-PSMA #3 are 30.2, 39.1, and 42.3 MPa, respectively; while those of mortars with cPAA-PSMA #4 are 31.3, 39.9, and 43.7 MPa, respectively. The compressive strength values of both cPAA-PSMA #3-added and cPAA-PSMA #4-added mortars are higher than those of plain mortars, with their values at 28 days of curing being higher by 31% and 35%, respectively, compared to that of plain mortar. These reasons will be mentioned again in results of FE-SEM and porosimetry analyses.

We also found an almost similar trend for flexural strengths for mortars with 1.0 wt%, on the core weight basis, of the various kinds of cPAA-PSMAs, as shown in Fig. 4. It seems that the flexural strengths of mortars with cPAA #1 and cPAA-PSMA #2 are similar to each other. The lowest flexural strength is for the 1.0 wt% cPAA-PSMA #2-added mortar, while the highest flexural strength is for the 1.0 wt% cPAA-PSMA #4-added mortar. Additionally, the flexural strength values are increased by 18% and 22% for mortars with cPAA-PSMA #3 and cPAA-PSMA #4, respectively, compared to that of plain mortar. These differences in compressive and flexural strengths of 1.0 wt% cPAA-PSMA #3 and cPAA-PSMA #4-added mortars are the result of the variations in the hydration reaction. The absorbent cPAA-PSMA #4, which has a thicker shell than cPAA-PSMA #3, has a longer hydration reaction time due to greater shell dissolution time. Consequently, cPAA-PSMA #4 starts to absorb excess water later than the other cPAA-PSMA absorbents, thereby securing longer working time.

4. FE-SEM Analysis of Cracked Mortars Cured for 28 Days

The FE-SEM images of cracked surfaces of 28 day-cured mortar, obtained from the compression strength tests, are indicated in Fig. 5. In each composite image, the part on the left is a low-magnification image, while the part on the right is a high-magnification image of the boxed portion of the left image. Acicular crystals of calcium silicate hydrate (C-S-H) can be seen in Fig. 5(a). It is known that C-S-H is composed of 50-60 vol% of hydrated Portland cement [17,18]. It is also known that crystals of C-S-H fill the pores of the Portland cement remaining after consumption of all water [19,20]. Fig. 5(b), which is the FE-SEM image of the mortar with cPAA #1, shows the cPAA #1 remaining after the swollen mortar was dried, covered and surrounded by acicular C-S-H crystals.

From Fig. 5(c)-(e), it can be observed that the added cPAA-PSMAs are filled among C-S-H crystals. As shown in Fig. 3 and 4, the reason for the mortars having cPAA-PSMA #4 exhibiting the highest strengths is the cross-linking between these filler C-S-H crystals [21,22].

As a corollary, such filling of pores leads to reduced pore volume, in turn leading to improved compressive strength of the mortar, as also established in earlier studies [21,22]. The pore of mortar's C-S-H crystals is filled by cPAA-PSMA #4, and as a result, the resultant pore size is smaller than that in the plain mortar, which is known from literature to be $\sim 1 \mu\text{m}$ [23]. Also, polymers with a carboxylic acid moiety have a monodentate coordination with Ca^{2+} in an aqueous solution of $\text{Ca}(\text{OH})_2$, and, therefore, effectively act as a cross-linking agent [24,25]. In our previous work [9], we found by Fourier transform infrared spectroscopy that added absorbents form carboxylate salts in a saturated aqueous solution of cement. In light of this, given that the main component of Portland cement is CaO [26,27] and its hydrate is composed of Ca^{2+} and OH^- , it can be concluded that the increased compressive strength of the mortars with absorbents is the result of coordination between Ca^{2+} and carboxylic acid moiety [25].

5. Porosimetry Analysis of Cracked 28 Day-cured Mortars

To measure the porosity and pore size distribution of cracked samples of plain mortar and mortars with added microcapsule absorbents that were cured for 28 days, a porosimeter was used. Fig. 6 shows the porosities and pore size distributions of plain mortar and mortars with 0.5 wt%, 1.0 wt%, and 1.5 wt% cPAA-PSMA #3. The specific volumes (ml/g) of pores $90 \mu\text{m}$ in diameter for plain mortar and mortars with 0.5 wt%, 1.0 wt%, and 1.5 wt% cPAA-PSMA #3 are seen to be 8.604×10^{-3} mL/g, 7.462×10^{-3} mL/g, 6.262×10^{-3} mL/g, and 6.176×10^{-3} mL/g, respectively. The volumes of $90 \mu\text{m}$ pores in mortars with 0.5 wt%, 1.0 wt%, and 1.5 wt% cPAA-PSMA #3 are lower than volume of such pores in plain mortar by 13.3%, 27.2%, and 28.2%, respectively. Also, the porosities of plain mortar and mortars with 0.5 wt%, 1.0 wt%, and 1.5 wt% cPAA-PSMA #3 were 21.2%, 20.7%, 17.7% and 16.3%, respectively. In comparison to the plain mortar, the pore volume and porosity decreased with increasing content of cPAA-PSMA #3 in mortar. These observations are the result of the PSMA shells of cPAA-PSMA #3 being hydrolyzed and dissolved in alkali cement pastes, and the concurrent filling of the cPAA core parts with C-S-H crystals through absorption of water and consequent swelling. In comparison to the plain mortar, the pore volume and porosity of mortars with 0.5 wt%

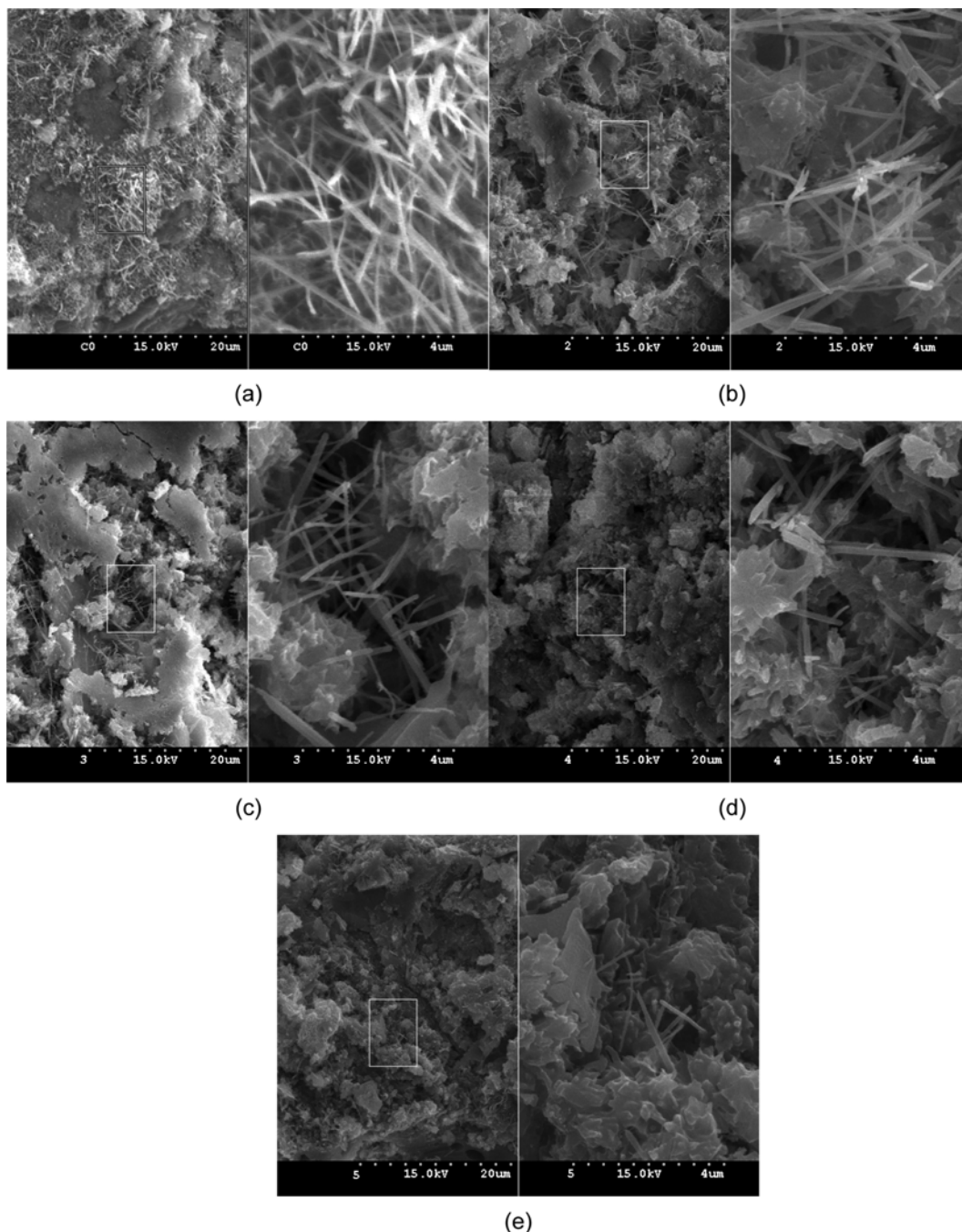


Fig. 5. FE-SEM images of surfaces of cracked specimens of plain mortar and mortars with absorbents. (a) Plain mortar, (b) mortar with cPAA #1, (c) mortar with cPAA-PSMA #2, (d) mortar with cPAA-PSMA #3, and (e) mortar with cPAA-PSMA #4.

cPAA-PSMA #3 was not large, because the amount of cPAA-PSMA available for the absorption of water was low. Also, the pore volume and porosity of mortars with 1.5 wt% cPAA-PSMA #3 were not much larger compared to those of mortars with 1.0 wt% cPAA-PSMA #3, because the amount of water absorbed in the cement paste was the same, despite the amount of cPAA being higher [2,3].

Mortars with 1.0 wt% cPAA-PSMA #2 and cPAA-PSMA #4 too were evaluated for their porosity and pore size distributions to compare with plain mortar and mortar with 1.0 wt% cPAA-PSMA #3.

Fig. 7 shows the porosities and pore size distributions of plain

mortar and mortars with 1.0 wt% cPAA-PSMA #2, cPAA-PSMA #3, and cPAA-PSMA #4. The relative amount of cPAA core in the cPAA-PSMA #2 absorbent is the largest among all microcapsule absorbents, while the relative amount of PSMA shell in cPAA-PSMA #4 is the largest. As shown in Fig. 7, volumes of pores 90 μm in diameter for plain mortar and mortars with 1.0 wt% cPAA-PSMA #2, cPAA-PSMA #3, and cPAA-PSMA #4 were 8.60×10^{-3} ml/g, 8.73×10^{-3} ml/g, 6.26×10^{-3} ml/g, and 6.39×10^{-3} ml/g, respectively. Also, volumes of pores 1 μm in diameter for plain mortar and mortars with cPAA-PSMA #2, cPAA-PSMA #3, and cPAA-PSMA #4 were

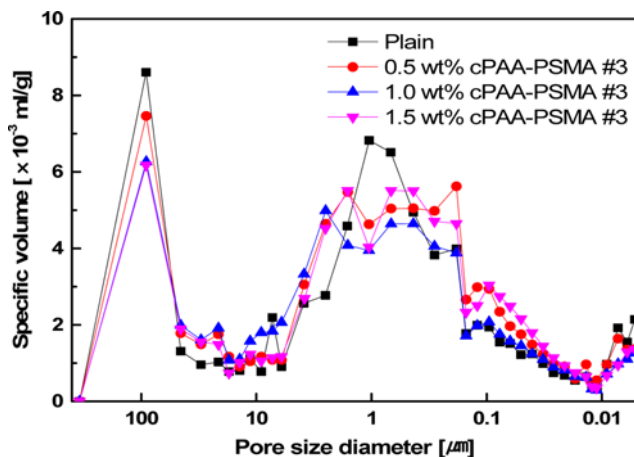


Fig. 6. Porosity and pore size distribution of plain mortar and mortars with 0.5 wt%, 1.0 wt% and 1.5 wt% core weight of cPAA-PSMA #3.

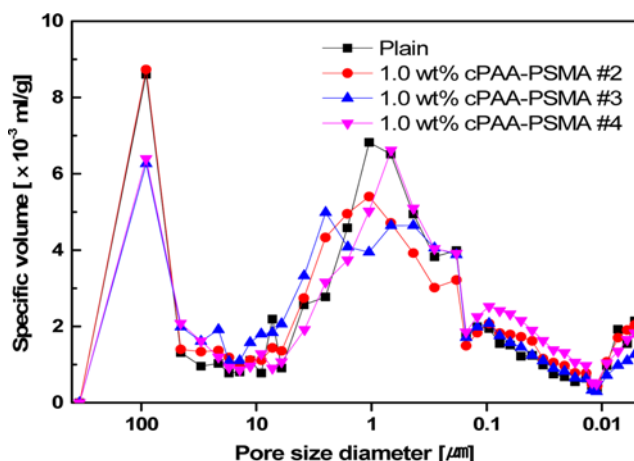


Fig. 7. Porosity and pore size distribution of plain mortar and mortars with 1.0 wt% core weight of cPAA-PSMA #2, cPAA-PSMA #3, and cPAA-PSMA #4.

6.82×10^{-3} ml/g, 5.40×10^{-3} ml/g, 3.95×10^{-3} ml/g, and 5.02×10^{-3} ml/g, respectively. The corresponding porosities of these mortars were 20.1%, 25.6%, 16.8%, and 16.15%, respectively. In comparison to the plain mortar, the pore volume of mortar with 1.0 wt% cPAA-PSMA #2 was not decreased significantly, because the shell part of the core-shell structure was not completely formed, as stated in the previous study [9], and consequently, cPAA-PSMA #2 swelled as soon as it was added to the cement paste. Therefore, the time required to fill the spaces between swollen cPAA-PSMA #2 structures by C-S-H crystals was insufficient. The mortar with 1.0 wt% cPAA-PSMA #4 exhibited smaller pores and a higher pore volume than the mortar with 1.0 wt% cPAA-PSMA #3, because the PSMA shell of the former, on account of being thicker, got swollen to a larger size leading to pores only 0.1 μm in diameter while its relatively smaller cPAA core compared to the latter resulted in 1 μm diameter pores [3].

From these observations, we concluded that the high compressive and flexural strengths of 1.0 wt% cPAA-PSMA #3-added mor-

tar are caused by its relatively smaller pores and pore volumes, which are evidenced by the corresponding FE-SEM images in Fig. 5.

CONCLUSIONS

The viscosity of cement pastes without microcapsule absorbent, and those of cement pastes with 1.0 wt% of cPAA #1, cPAA-PSMA #2, cPAA-PSMA #3, and cPAA-PSMA #4, were compared. Viscosity of the cement paste without absorbent increased slowly, while the viscosities of cPAA #1- and cPAA-PSMA #2-added cement pastes increased relatively faster. In contrast, the cement pastes with 1.0 wt% cPAA-PSMA #3 and cPAA-PSMA #4 on the core weight basis showed a slower increase in viscosity till 30 minutes and 90 minutes after their addition, respectively. After that, they both showed a rapid increase in viscosity. Therefore, a maximum working time of 90 minutes can be secured by delaying water absorption when using cPAA-PSMA #4 absorbents.

The compressive and flexural strengths of mortars with 1.0 wt% of cPAA-PSMA #4 absorbent on the core weight basis showed an increase of 35% and 22%, respectively, while those with 1.0 wt% of cPAA-PSMA #3 showed an increase of 31% and 18%, respectively, compared to plain mortar. Also, upon investigating the morphology of the mortar after the addition of cPAA-PSMA #4, it was observed that the absorbent had filled the spaces between C-S-H crystals. The evaluation of the corresponding porosity and pore size distribution, with the dissolved shell of cPAA-PSMA #4, showed a filling pore size $< 0.1 \mu\text{m}$, which affected the overall strength of the mortar. Through this research, we found that cPAA-PSMA #4, which was synthesized with a 1 : 1.5 cores:shell mass ratio, showed a well-formed core-shell structure, and that it is possible to secure 90 minutes of working time with this absorbent through the delaying of water absorption.

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