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Assessment of self-healing behavior of polypropylene fiber-reinforced cement mortar with crystalline admixture: the effects of crack widths, cracking ages, and external conditions

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Abstract. Crystalline admixture (CA) is an effective self-healing agent for mortar. However, the effects of crack parameters (i.e. crack width and cracking age) and the service environment on the self-healing behavior of CA-containing mortar are not well understood. Herein, the self-healing behavior of mortar containing a self-developed CA was assessed by testing strength recovery, impermeability recovery, and crack closure in pre-cracked specimens. Three initial crack widths (0.2, 0.3, and 0.4 mm), five cracking ages (3, 7, 14, 28, and 56 days), and four external exposure conditions (humidity chamber, air exposure, water immersion, and wet-dry cycles) are investigated. Furthermore, the influence of different external conditions on the healing products at the region of crack and the pore structure of hardened paste containing CA are studied. The results show that adding 4.54% CA into mortar allows rapid healing of 300 μm-wide cracks. Although wider cracks (400 μm) are more difficult to heal, the sorptivity coefficients of the mortars with 400 μm-wide cracks after healing decrease. When the cracks are produced at an earlier age, the pre-cracked specimens have higher recovery ratios of strength and impermeability after healing, and the specimens pe-cracked at a later age still have acceptable compressive strengths after healing. The analysis shows that the strengths and impermeabilities of pre-cracked mortars containing CA exposed to the four external conditions are all recovered. The best self-healing performance is observed for the specimens exposed to water immersion and wet-dry cycles conditions. Somewhat less good self-healing was observed in the specimens exposed to humid chamber condition, while the worst self-healing performance was in the specimens exposed to air exposure condition. This study provides a theoretical basis for the application of novel CAs in cement-based materials.

Keywords: Self-healing behavior; mortar; crystalline admixture; crack; permeability

1. Introduction

Cracks are inevitable in concrete structures either due to external load or environmental exposure [1,2]. Cracks provide channels for the transmission of harmful substances, and may seriously affect the durability and service life of concrete structures [3]. Different methods for crack repair have been developed, and they mostly follow the sequence of monitoring, detecting, and repairing [4]. However, in the case of large-scale concrete structures, the crack detection and repair are difficult and costly, and the manual repair of cracks in underground and underwater structures is difficult [5,6]. These issues are driving the development of self-healing cement-based materials (CBMs) [4,7]. Self-healing CBMs mainly refer to the cement-based composites that can heal small cracks autogenously and autonomously without any external diagnosis or manual intervention [8]. The inherent self-healing ability of CBMs allows some cracks to heal autogenously, but the self-healing processes without stimulation are evidently slow and limited [4]. Li et al. [9] suggested that the maximum crack width that could be healed in cement-based engineered cementitious composite without activators is 50 μm. Therefore, the potential of various components to achieve self-healing functionality has been investigated, such as capsules, bacteria, and supplementary cementitious materials (SCMs) [4]. The incorporation of capsules or bacteria into CBMs generally improves the self-healing efficiency and may result in healing cracks of up to 300–400 μm [4]. However, the addition of capsules commonly results in lower concrete strength [10], and the activity of bacteria is greatly affected by the high alkalinity in the concrete environment [11,12]. The physical stability and low cost of SCM enable it to be widely used in self-healing CBMs, but the increase of self-healing efficiency due to SCM incorporation is usually not as good as the increase in self-healing efficiency due to bacteria or capsule incorporation. To further improve the healing efficiency and application feasibility of admixtures component, additional active chemicals need to be added to the self-healing additive.

Crystalline admixture (CA) has a twofold effect of reducing the permeability and self-healing of the cracks in concrete, so it can be widely used in waterproofing and reducing permeability of concrete structures [13]. The ACI 212.3 R-16 classifies CA under the subcategory of permeability-reducing admixtures for structures exposed

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to hydrostatic conditions [14]. Although CA has been increasingly used as a permeability reducing agent, the vast majority of CA's are commercial products, and the chemical composition is mostly not disclosed. It is a general agreement that CA is a mixture of different compounds, including silicates, pozzolans, and active chemicals [15]. Moreover, there are also some self-developed formulations based on carbonates, silicates, aluminates, glycine, and sodium acetate [15]. Compared with other waterproofing or hydrophobic products (such as asphalt and rubber), CA is highly hydrophilic and can react with cement hydration products [16,17]. Besides, CA can promote the formation of C–S–H gels and $CaCO_3$, which effectively refines the pore structure, thus significantly reducing the permeability of concrete [18,19]. Several studies reported the reduction in water permeability and the improvement in mechanical properties of concrete after CA addition. On the one hand, the waterproofing ability of concrete containing CA was significantly improved, adding CA into concrete reduced the depth of water penetration by about 40% [20]. On the other hand, the 7-day and 28-day compressive strengths of wet-cured concretes containing CA were at least 14% higher than the plain concrete [21]. This has been attributed to the homogeneous dispersion of CA in concrete during the mixing process, which not only refines the pore structure but also improves the microstructure compactness by acting as a filler [21]. Therefore, CA is low cost, easily available, applied to CBMs in powder form, and has a good compatibility with CBMs [16]. However, the effect of CA on the self-healing behavior of CBM is not clear and further studies are still needed.

For self-healing CBMs, the crack parameters (i.e. crack width (CW) and cracking age) are very critical influencing factors [4,22]. Several studies have explored the CWs that can be healed by CA addition. Jaroenratanapirom and Sahamitmongkol [23,24] experimentally confirmed that the CA-containing mortar could quickly heal cracks below 50 μm, but has limited healing effect on cracks above 300 μm. Sisomphon et al. [25] claimed that the pre-cracked mortars containing CA were completely healed for CW range of 200–250 μm within 28 days; in the reference (plain) mortar, only cracks of up to 150 μm were healed. Ferrara et al. claimed [26] that CA could promote crack closure in the width range of 300–500 μm, while De Belie et al. [27] indicated that the crack width that can be healed by CA was limited to the range of 100–150 μm. Clearly, the maximum reported healable crack width varies in different studies, which may be due to differences in the specific components of CA. In addition, several researchers have investigated the influence of cracking ages on the self-healing properties of CA-containing CBMs. Some researchers investigated the self-healing behaviors of CA-containing mortars at different cracking ages (7 and 28 days), and found that the cracks induced at 7 days had a better self-healing effect than those induced at 28 days, which could be partly attributed to the further hydration of unhydrated phases [28]. However, Reddy and Ravitheja, [29] and Li et al. [30] obtained the opposite experimental results, and concluded that delaying the cracking ages increased the self-healing effect of CA-containing concrete, without explaining the governing mechanisms. Therefore, the influence of cracking ages on self-healing behavior of CA-containing CBMs needs further study. Furthermore, except for the crack parameters, the self-healing behavior of CA-containing CBMs may also be affected by external environments. Sisomphon et al. [31] investigated the strength recovery of strain hardening cement composite containing CA under water immersion (WI), wet/dry cycling, and air exposure (AE) conditions. The results indicated that the wet/dry cycling had the best healing effect, while air exposure resulted in no significant healing. Ferrara et al. [26] investigated the strength recovery of concrete containing CA under water immersion condition and found that CA incorporation accelerated the crack healing process and restored the load-bearing capacity and bending stiffness. Roig-Flores et al. [32] studied the mechanical recovery of concrete containing CA under four external conditions. The four conditions in increasing order of impermeability healing ratios of mortars were AE < humidity chamber (HC) < water contact < WI. These researchers have done numerous efforts on the application of CA in self-healing CBMs, but the existing studies have generally focused on only one of the three factors (CWs, cracking ages, and external environments). Therefore, a study with systematic focus on the effects of both crack parameters and external environments on self-healing behavior of CA-containing CBMs is still needed.

To explore the feasibility of CA in enhancing the self-healing ability of cement components, the effects of CA on the self-healing behaviors of pre-cracked mortar specimens (PMSs) were investigated separately for different crack widths (CWs), cracking ages, and external conditions. The healing of cracks on the mortar surface was evaluated by the variation of CW, and the recovery of properties was evaluated by strength and impermeability with various media. The physical closure of surface cracks and the crack morphology inside the PMSs were observed by optical microscopy and scanning electron microscopy (SEM), respectively. Moreover, the effect of different external conditions on the internal pore structure of mortar containing CA was characterized by mercury intrusion porosimetry (MIP).

2. Experimental program

2.1. Materials and proportions

The mortar was prepared by mixing cement, sand, water, polypropylene (PP) fiber, and superplasticizer (SP). The cement used in this study was 42.5 ordinary Portland cement. The purpose of this project was to explore the self-healing capabilities of PMSs, PP fiber could provide a favorable action both to control the CW during the pre-cracking process and to enhance the self-healing ability of mortar. The high-strength PP fiber with a length of 8–10 mm was used. Moreover, to improve the fluidity of the mixture, SP with a solid content of 40% was also added.

CA generally includes crystallization reactants that can generate crystals, calcium ion chelators, and calcium ion compensators [16]. The basic materials of active chemicals of CA selected for this study were Na_2CO_3, Na_2SiO_3, $Ca(HOOC)_2$, nano-silica (NS), triethanolamine (TEA), and glycine, which were identified based on the previous study [33]. Among the materials, Na_2CO_3 and Na_2SiO_3 were auxiliary precipitating agents, $Ca(HOOC)_2$ was a calcium ion supplement, and TEA and glycine were metal ions chelators. To combine with Ca^{2+} to generate more C–S–H gels, NS was selected as a component of CA. The incorporation of each active chemical above was set in the following content (wt. %): 1.0%Na_2CO_3, 1.0%Na_2SiO_3, 0.5%$Ca(HCOO)_2$, 1.0%NS, 0.04%TEA, and 1.0%glycine. The contents of the active chemicals were calculated as the weight percentage of cement.

2.2. Specimen preparation

The mortar was modified by adding CA at 4.54% by weight of cement, and its self-healing behavior was compared with the plain mortar. Table 1 lists the mixture proportions and the compressive strengths of mortars cured in standard curing condition (20 ± 2 °C, 95 ± 3% RH) for 3, 14, 28, and 56 d. The specific mortar mixing process and the curing regime were the same as in our previous study [33]. In the mixture proportion, the mortar without CA is noted as ‘WCA,’ and the mortar added with CA is noted as ‘ACA.’

2.3. Methodology and parameters design

2.3.1. Pre-cracking process

To investigate the maximum CW that could be healed by CA, cylindrical mortar specimens (Φ100 × 50 mm) were subjected to pre-cracking immediately after standard curing for 3 days to produce different initial CWs (0.2, 0.3, and 0.4 mm). To further illustrate the effect of cracking age on the self-healing behavior of mortar containing CA, surface cracks were produced at different ages (3, 7, 14, and 28 days). Finally, all the PMSs were placed in standard curing condition for 28 days for healing. In this study, the PMS of mortar added with CA is noted as ‘PACA,’ and the PMS of mortar without CA mortar is noted as ‘PWCA.’

All cylindrical specimens were pre-cracked, and the CW was controlled as shown in Figure 1. This method of generating cracks and width control has been widely used [25,34]. These specimens were cured in standard curing conditions until the test age, and then they were split in half with a hydraulic press. The two pieces of each specimen were held together by PP fibers. Then, PMSs were placed in a rubber mold to hold the split halves in place. Each rubber mold of each specimen was fastened with a stainless-steel clamp, and cracks of different widths (0.2, 0.3, and 0.4 mm) were prepared by adjusting the stainless-steel clamps. CWs were measured and recorded at 25 mm intervals on the surface of each specimen. Finally, the specimens with different initial CWs were continuously cured in standard curing condition for 28 days.

2.3.2. Exposure simulation

To determine the influence of external conditions on the self-healing behavior of PACA, this study simulated different environmental conditions to further analyze the factors affecting the self-healing properties of mortar. Each exposure condition was designed to simulate different external conditions of practical constructions.

Humidity chamber (HC): simulated mortar elements in an environment with high humidity but without direct water contact. Specimens were stored in a standard humidity chamber (20 ± 2 °C and 95 ± 3% RH).

Air exposure (AE): simulated mortar elements in the air. Specimens were stored in normal laboratory conditions (20 ± 2 °C and 40 ± 5% RH).

Water immersion (WI): simulated mortar elements submerged under water. Specimens were immersed in tap water at 20 ± 2 °C and the soaking water was renewed every 7 days. The height of the water layer was maintained at 2–3 cm above the upper surface of the specimens.

Wet-dry cycles (WC): simulated mortar elements that were used in areas of high rainfall frequency. Specimens were stored under water immersion for 12 h and followed by air curing (20 ± 2 °C and 40 ± 5% RH) for 12 h. Every 24 h was set as a wet-dry cycle.

2.3.3. Compressive strength and strength recovery ratio (SRR)

The compressive strength test was carried out on cubic mortar specimens (40 × 40 × 40 mm) with a loading speed of 0.005 mm/s. The average of the test result obtained from six cubic specimens of each group was taken as the compressive strength. The data deviating from the average value by 10% were removed.

Moreover, SRR was used to assess the self-healing capability and healing efficiency of internal cracks in mortar containing CA [16]. After standard curing to a certain age (3, 14, 28, and 56 days), six cubic mortar specimens of each group were used for the compressive strength test, and the failure stress value was recorded as P_0. Then, another six specimens with the same age were pre-loaded. The pre-loading stress was 70% of the failure stress ($0.7\,P_0$), and the load was removed after holding for 15 s.

Table 1. Mixture proportion of mortar (wt.%).

Group	Cement	Sand	Water	SP	CA	PP fiber (Vol. %)	Compressive strength (MPa)			
							3 d	14 d	28 d	56 d
WCA	100	200	40	0.2	0	0.2	18.6	31.2	35.9	38.9
ACA	95.46	200	40	0.4	4.54	0.2	26.2	46.4	49.7	54.1

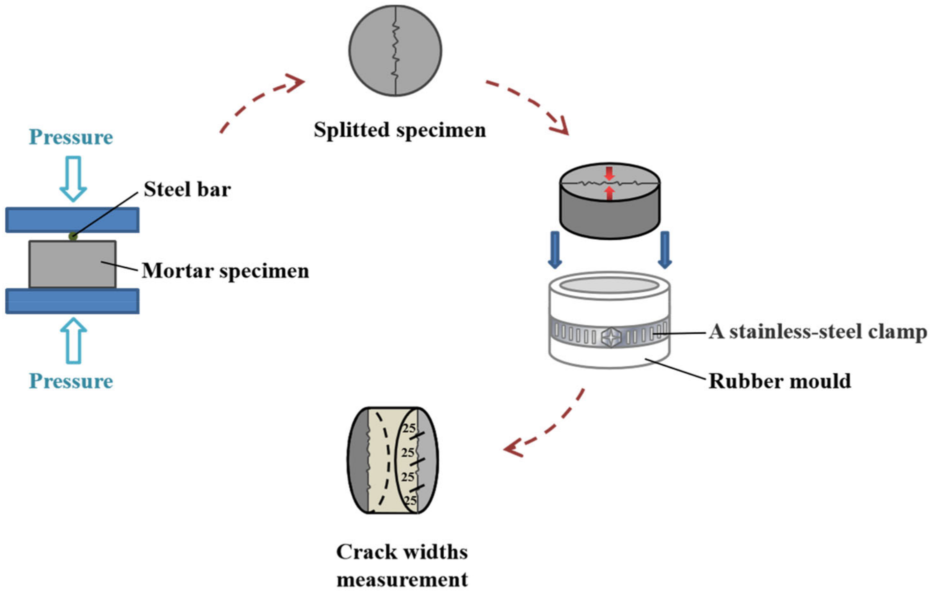

Figure 1. The specimen cracking and CW controlling.

In the pre-loading process, a mechanical strength test device (TYE-1000E, produced by Wuxi jianyi instrument and machinery Co., ltd., China) was used. After pre-loading, specimens were continuously placed in standard curing condition for 28 days to start self-healing. Finally, the compressive strength of the mortar after healing was tested, and the value was recorded as P_1. SRR is calculated by Equation (1).

$$SRR = \frac{P_1}{P_0} \times 100\% \quad (1)$$

where P_0 is the compressive strength of specimen before healing (MPa), and P_1 is the compressive strength of pre-loaded specimen after healing (MPa).

2.3.4. Permeability and impermeability recovery ratio (IRR)

Permeability test can indirectly reflect the healing of cracks inside the mortar, and the test samples were pre-cracked cylindrical mortar specimens (Φ100 × 50 mm) before and after healing. Using chloride ions, air, and water as osmotic media, the permeability of mortar was tested with reference to NT Build 492, CNS JTJ270-89, and ASTM C1585, respectively. The chloride ion permeability coefficient, gas permeability coefficient, and sorptivity coefficient were calculated directly as described in [33]. Herein, the capillary water absorption (CWA) and sorptivity coefficient from water absorption test were used to evaluate the water permeability of pre-cracked mortar before and after healing.

IRR was used to evaluate the self-healing capability of PACA. The permeability coefficient of mortar after the pre-cracking process was first tested, and recorded as C_0. At the end of the healing process, the permeability of the specimen would be tested again, recorded as C_1. IRR is then calculated as Equation (2).

$$IRR = \frac{C_0 - C_1}{C_0} \times 100\% \quad (2)$$

where C_0 is the coefficient of specimens after the pe-cracking process, and C_1 is the coefficient of the specimen after the healing process.

2.3.5. Surface crack patterns

To investigate the self-healing behavior of surface cracks, an optical microscope (MG10085-2, China) was used to measure the cracks along the surface crack path. By tracking the markings done before, the changes in CWs and morphology were observed and recorded periodically.

2.3.6. SEM

SEM was used to capture the microstructure of the self-healing products of PACAs. First, approximately 10 × 10 mm flake samples were taken from both sides of the unclosed cracks of the PACAs, followed by immersion in isopropyl alcohol for 7 days to stop hydration. The samples were then dried in a vacuum desiccator for 7 days. Since CBMs are non-conductive, the surface of the dried sample was uniformly sprayed with platinum to increase electrical conductivity. The type of SEM used was tungsten filament SEM, and the JSM-649LV high vacuum tester (produced by Japan Electron Optics Laboratory co., ltd., Japan) with the accelerating voltages of 15 and 20 kV was used for observation.

2.3.7. MIP

The internal pore structure of paste containing CA under different external conditions was characterized by MIP. The test equipment was an Autopore IV 9500 mercury piezometer with a maximum working pressure of 346 MPa, which allowed the intrusion of mercury into small pores with a diameter of 5 nm. The paste specimen pre-cracked at 3 days was cured in different external conditions for 28 days, and then a sample of approximately 8 × 8 × 8 mm in size was taken from the interior of the hardened paste. The samples were immersed in isopropyl alcohol for 7 days to terminate hydration, and then these were dried in a vacuum desiccator for 7 days before testing.

3. Results and discussion

3.1. Influence of CWs on self-healing behavior of mortar

3.1.1. Water absorption test

After healing in standard curing condition for 28 days, the CWAs of PMSs with different initial CWs were measured and are shown in Figure 2. The reduction in total CWA differs between PWCA and PACA when the initial CW varies. After CA addition, the total CWA of the specimen with an initial CW of 0.4 mm decreases by 51.9%, while the total CWA of the specimen with an initial CW of 0.2 mm decreases by 76.6%. The decrease in total CWA reflects the densification of microstructure due to the formation of healing products and the closure of cracks. It also leads to the conclusion that CA is more effective for healing small cracks and relatively weak for healing large-sized cracks (0.4 mm). For these three CWs, the total CWAs of the specimens containing CA after healing are significantly reduced, implying that CA addition accelerates the self-healing process. The PACA with an initial CW of 0.4 mm has the largest total CWA, and the total CWA of the specimen is reduced by 40.0 and 57.6% when the CWs are reduced to 0.3 and 0.2 mm. This indicates that, as the CW decreases, the total CWA of the specimens also decreases. For PACAs with different initial CWs, the specimen with 0.3 mm crack shows a 41.6% increase in total CWA compared to the specimen with 0.2 mm crack, and the specimen with 0.4 mm crack has a 66.6% increase in total CWA compared to the specimen with 0.3 mm crack. This indicates that equal content of CA is less effective in promoting the self-healing behavior of mortars with larger-sized cracks compared to mortars with small cracks. Obviously, CA addition has a facilitative effect on the self-healing behavior of mortar, and when the initial CW does not exceed 0.3 mm, the PACA has a good self-healing effect with a 69.4% reduction in total CWA over the PWCA.

Figure 3 shows the sorptivity coefficients based on a linear fit of the statistical data in Figure 2. CA significantly reduces the sorptivity coefficients of the specimens. When the initial CWs are 0.4, 0.3, and 0.2 mm, CA incorporation reduces the sorptivity coefficients of the specimens by 47.6, 66.4, and 75.4%, respectively. This indicates that CA can promote the reduction of the sorptivity coefficient, and CA has a more positive effect on the self-healing performance of mortar when the CW is smaller. For all the specimens, the sorptivity coefficient decreases with the decreasing initial CWs. For the PWCAs, the differences in sorptivity coefficients for specimens with different CWs are not significant, with the sorptivity coefficient of specimen with 0.2 mm crack being only 4.6% lower than that of specimens with 0.4 mm crack. However, for the PACAs, the sorptivity coefficients of specimens with 0.3- and 0.2-mm cracks are 37.1 and 55.2% lower than that of specimen with 0.4 mm crack. This indicates that the CA incorporation leads to a very rapid reduction of the sorptivity coefficient, and the initial CW has a strong influence on the water impermeability of PACA. When the CA content is constant and the initial CW is smaller, the mortar containing CA has a greater self-healing behavior.

3.1.2. Crack closure behavior

The statistical results of the self-healing behavior of surface cracks with different widths measured using optical microscopy are shown in Figure 4. The average CW measured in three different locations was recorded. For

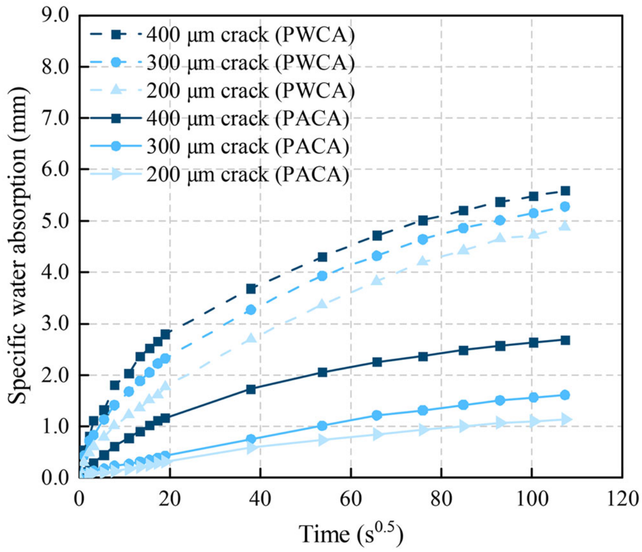

Figure 2. CWAs of PMSs with different initial CWs after healing.

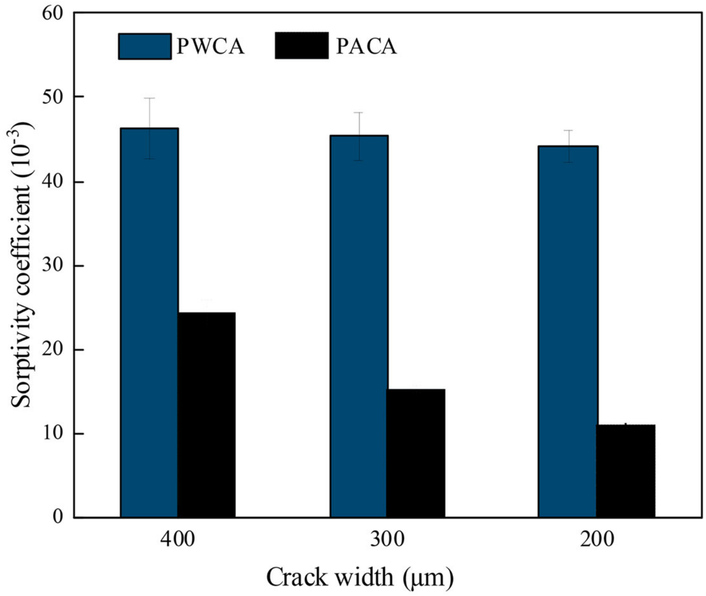

Figure 3. Sorptivity coefficients of PMSs with different initial CWs after healing.

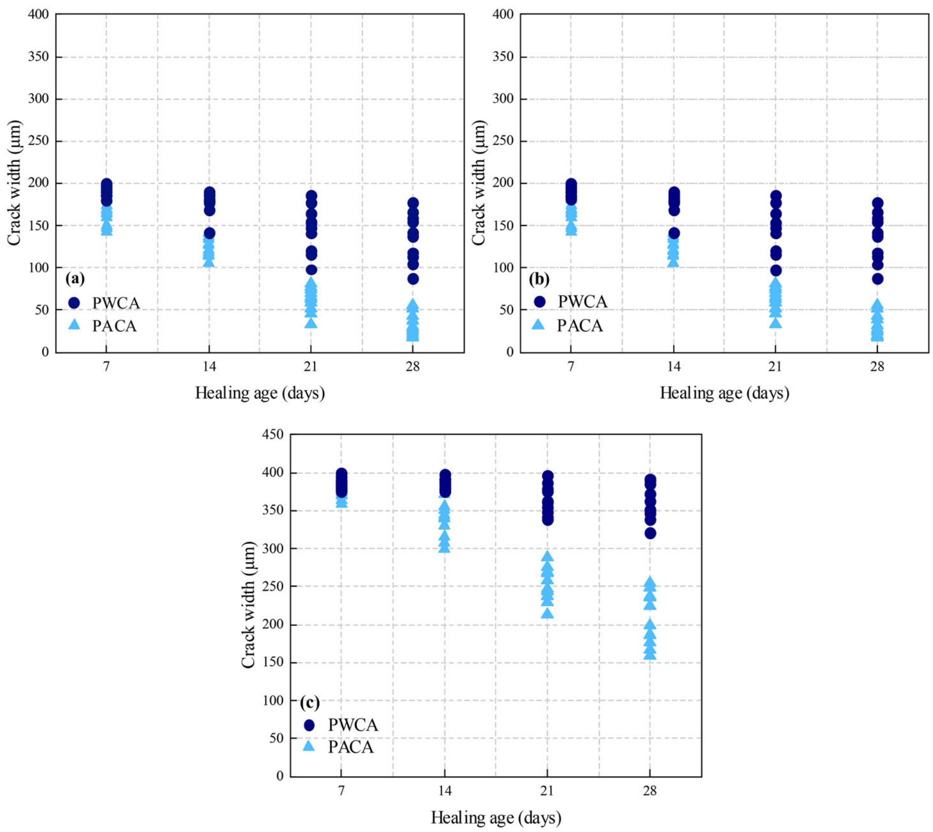

Figure 4. Statistical results variation with healing ages for different initial CWs, (a) 200, (b) 300, and (c) 400 μm.

each CW set (0.2–0.4 mm), 10 samples with cracks were prepared.

As shown in Figure 4, the CWs of all samples gradually decrease with increasing healing age, regardless of whether they contain CA or not. Figure 4(a) shows that the average CWs of the PWCA after healing for 7, 14, 21, and 28 days are reduced by 5.0, 11.5, 27.2, and 32.2% relative to the initial CWs, respectively. Furthermore, the average CWs of the PACAs after healing for 7, 14, 21, and 28 days decrease by 19.0, 37.9, 69.2, and 83.5%, respectively, relative to the initial CWs (Figure 4(a)). The average CWs of the PACAs after healing for 7, 14, 21, and 28 days are 264, 224, 150, and 60 μm, respectively, which are reduced by 6.4, 17.6, 37.5, and 72.5% relative to the average CWs of the PWCAs after healing (Figure 4(b)). This is because, as the healing age increases, the unreacted components in contact with water can generate additional reaction products to promote the self-healing behavior of surface and internal cracks. After healing for 28 days, cracks are recovered to varying degrees, and it is expected that the cracks can be healed better as the healing age increases. Furthermore, the surface cracks are in direct contact with air, thus CO_2 from the air can enter the cracks, CO_2 dissolves in water and combines with Ca^{2+} at the cracks to form $CaCO_3$ due to the higher humidity at the cracks, which is beneficial to crack healing.

Moreover, the average CWs of the PWCAs are 1.2 and 1.4 times as large as those of the PACAs at the healing ages of 7 and 14 days, respectively (Figure 4(a)). However, when the healing ages reach 21 and 28 days, the average CWs of the PWCAs are 2.4 and 4.1 times as large as those of the PACAs (Figure 4(a)). Figure 4(b,c) show a similar pattern, i.e. the PWCAs and PACAs have similar average CWs at 7 and 14 days, but when the healing ages increase to 21 and 28 days, the average CW of the PWCA is much larger. This may suggest that CA makes a greater contribution to the self-healing behavior of mortar at a late healing stage (21–28 days). This may be because CA promotes the self-healing behavior of mortar in both early and late healing stages; although both cement and CA promote the self-healing of cracks, CA makes a greater contribution in the late healing stages. The inherent self-healing capability of mortar is limited and gradually decreases with the increasing healing ages. In contrast, CA incorporation significantly improves the self-healing behavior of mortar, which is less affected by the increasing healing ages and still demonstrates excellent efficiency of crack closure in the late healing stage.

In conclusion, rapid crack healing is promoted by cement hydration in the early healing stages. CA accelerates crack closure in both the early and the late healing stages, and CA plays a minor role in early healing stages but a major role in late healing stages. In the late healing stage, the content of unhydrated phases in mortar is evidently low, however, CA components potentially react with hydration products to promote further formation of healing products, thus making CA play a dominant role in the self-healing behavior of mortar. Moreover, the results above indicate that cracks of different widths have different healing performance, and the further mechanistic elaboration is shown in Figure S1.

3.2. Influence of cracking ages on self-healing behavior of mortar containing CA

3.2.1. Compressive strength

The compressive strengths and SRRs of PACAs at different cracking ages after healing are shown in Figure 5. The compressive strengths of PACAs all increase with the increasing cracking ages. The specimen pre-cracked at 3 days after healing has the lowest compressive strength, which is 38.0 MPa. The compressive strength of the specimen pre-cracked at 14 days after healing is 48.4 MPa, and the specimens pre-cracked at 14, 28, and 56 days after healing show little difference in compressive strengths. Contrary to the changing trend of compressive strength variations with cracking ages, the SRRs decrease with the increasing cracking ages. The SRR of the 3-day PACA reaches 144.84%, and the SRR of the 14-d PACA is also higher than 100%. This may imply that specimens pre-cracked at an early age have superior self-healing properties when the healing age is consistent. For specimens pre-cracked at an early age, there are more unhydrated phases in the matrix that promote crack healing [35].

Though the SRRs of specimens pre-cracked at 28 and 56 days after healing are both lower than 100%, their compressive strengths after healing still reach 48.6 and 49.2 MPa, respectively. Although the SRR decreases with the increasing cracking age, there is little difference in the compressive strengths of the specimens pre-cracked at 28 and 56 days after healing. This is because, as the cracking age increases, the internal microstructure is denser and the bonding performance of fiber and matrix is enhanced. More importantly, TEA and glycine in CA are efficient metal ion chelators that can combine with Ca^{2+}, Mg^{2+}, and Zn^{2+} ions from the pore solution to form unstable chelate compounds [33]. When these chelate compounds reach the regions where hydration products are abundant, the anions in the unstable chelate compounds will be replaced by silicate (SiO_3^{2-}) and aluminate (AlO_2^{-}) ions due to the difference in solubility and stability of the products [16]. The generated stable and water-insoluble C–S–H gel fills the pores and cracks inside the mortar [16]. Finally, the anions in the unstable chelate compounds become free again, penetrate and circulate with water, and

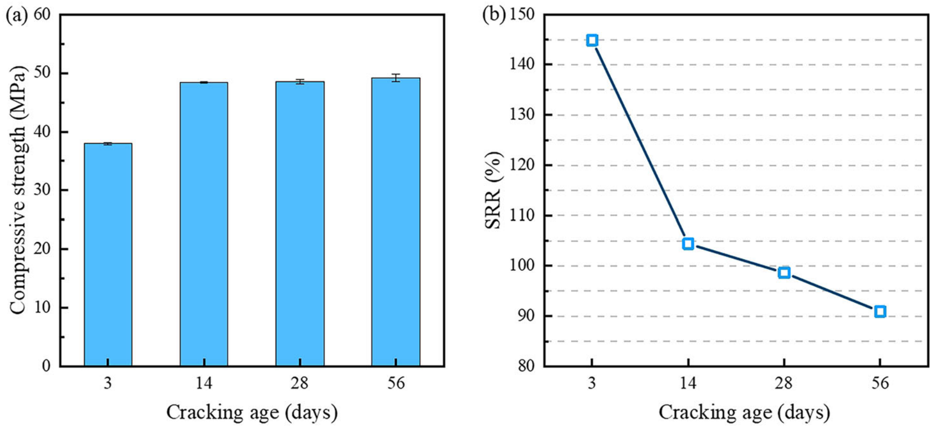

Figure 5. Compressive strengths and SRRs of PACAs at different cracking ages after healing.

continue to diffuse in the pore solution of mortar. It may explain the promotion of self-healing behavior by CA exhibits long-term effectiveness.

After healing for 28 days, the SRR of the specimens pre-cracked at 56 days is reduced to 90.93%, and the compressive strength of the PACA after healing is lower than that of the specimen without pre-loading. This indicates that CA promotes the self-healing of mortar when the cracking age is late, but the compressive strength of the PACA cannot recover after healing to the compressive strength of the specimens not subjected to pre-loading. This may be because the main components of healing products are weaker than the C-S-H gels from the cement hydration [32]. Even if the C–S–H gel is formed inside the crack due to the hydration of unhydrated phases, the bond between the crack surface and the new C-S-H gel is most likely weaker compared with the strength of the original matrix [9,36].

3.2.2. Chloride ion permeability

The chloride ion permeability coefficients (CPCs) and IRRs of PACAs at different cracking ages before and after healing are given in Figure 6. The CPCs of PACAs after healing increase with the increasing cracking ages. Among the PACAs before healing, the specimen pre-cracked at 28 days shows the highest chloride ion resistance, and the CPCs of the specimens pre-cracked at 14 and 28 days are similar. In addition, the 3-day PACA before healing has the highest CPC, and the CPC of the 3-day PACA is 1.1 and 1.6 times as high as that of the 7-day and 14-day PACAs, respectively. This is due to the early cracking age and more unhydrated phases in the early healing stages, making the matrix less resistant to chloride ingress. For PACAs with different cracking ages, the CPCs are all significantly decreased after healing. The 3-day PACA after healing has the lowest CPC, and the CPC of the 3-day PACA after healing is 1.7, 5.3, and 6.6% lower than that of the 7, 14, and 28-day PACAs after healing, respectively (Figure 6). Besides, the IRRs of PACAs decrease with the increasing cracking ages, with the highest for the specimen pre-cracked at 3 days (65.0%) and the lowest for the specimen pre-cracked at 28 days (38.7%). This can be attributed to the high concentration of TEA in CA at an early cracking age, TEA can promote the hydration of tricalcium silicates in cement clinkers and accelerate the self-healing of cracks [37,38]. Besides, TEA affects the process of $Ca(OH)_2$ (CH) formation and the morphology of synthesized CH crystals [39,40]. The different morphologies of CH crystals exhibit different reactivity with CO_2, leading to accelerated precipitation of $CaCO_3$ and gradually blocking the cracks [41]. Moreover, though the CPCs seem to show a weakening trend with increasing cracking age, it basically remains near 10.0×10^{-12} mm^2/s. The cracks can cause a dramatic increase in the permeability of mortar, and the permeability of cracked mortar is several orders of magnitudes higher than that of uncracked mortar. Therefore, healing cracks is the key to improving the resistance of mortar to chloride ingress, and the further mechanistic elaboration is shown in Figure S2.

3.2.3. Gas permeability

The gas permeability coefficients (GPCs) and IRRs of PACAs at different cracking ages before and after healing are shown in Figure 7. Compared with chloride ion ingress, air as the osmotic medium has smaller molecules, and the self-healing effect of CA on the mortars at different cracking ages might be more sensitive to gas permeability. Therefore, the specimens pre-cracked at 3 days have not been tested due to their excessive gas permeability.

For all the PACAs before healing, the specimen pre-cracked at 7 days has the highest GPC, with the GPC being 1.3 and 1.7 times as high as those of the specimens pre-cracked at 14 and 28 days. Nevertheless, the CPCs of the specimens pre-cracked at 14 and 28 d before healing are close (Figure 5), but the GPC of the specimen pre-cracked at 14 d is lower by 24.7% compared to that of the specimen pre-cracked at 28 days (Figure 7). It is well known that the permeability of mortar is not only related to the matrix compactness but is significantly affected by defects and damage (e.g. pores and cracks). The GPCs of PACAs after healing decrease with the increasing cracking ages. The specimen pre-cracked at 7 days after healing have the lowest GPC, with the GPC that is 11.3 and 39.0% lower than those of the specimens pre-cracked at

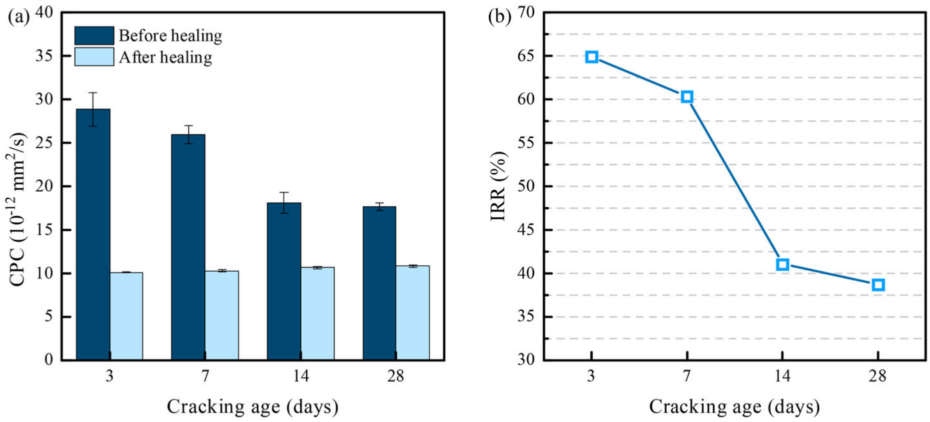

Figure 6. CPCs and IRRs of PACAs at different cracking ages before and after healing.

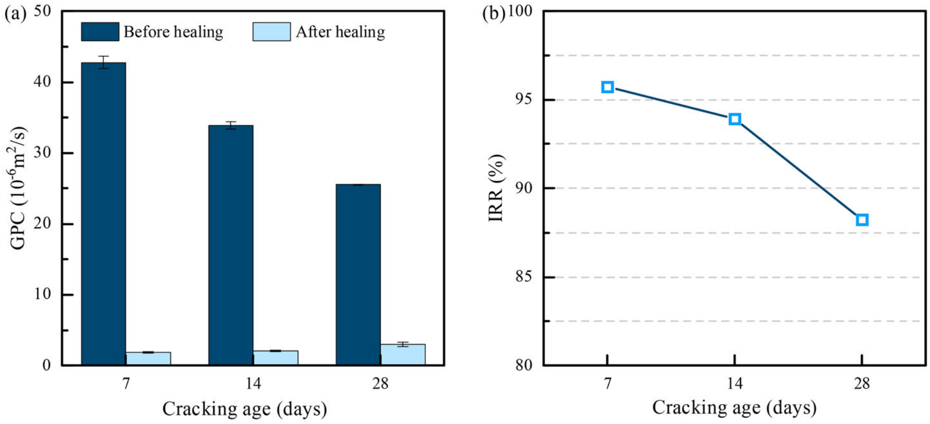

Figure 7. GPCs and IRRs of PACAs at different cracking ages before and after healing.

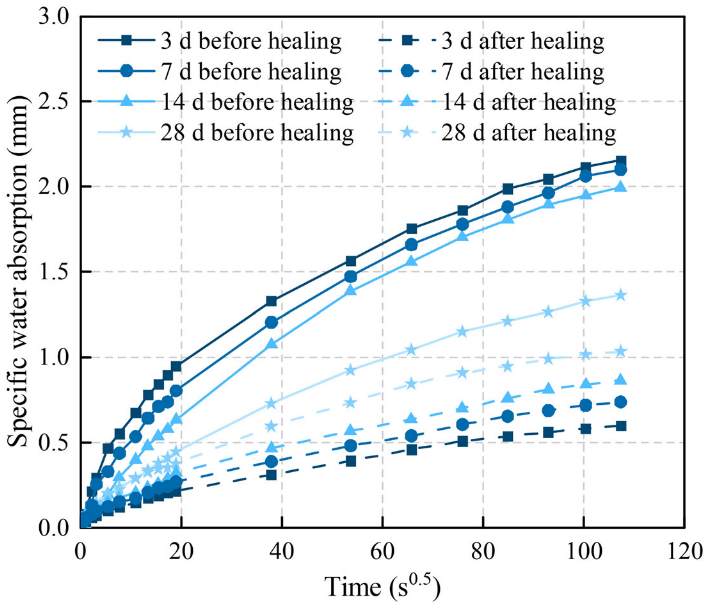

Figure 8. CWAs of PACAs at different cracking ages before and after healing.

14 and 28 days after healing, respectively. Moreover, the specimen pre-cracked at 7 days after healing has the highest IRR at 95.7%. This indicates that CA contributes to the self-healing of cracks in mortar, and it is more pronounced for specimens pre-cracked at an early age. Due to the early cracking age, there are more unreacted phases at the crack region, which can generate a large amount of healing product to fill the crack during the subsequent healing process, thereby hindering the passage of gas and restoring the impermeability of mortar.

Notably, although the specimen pre-cracked at 28 days after healing has the lowest GPC, the specimen achieves the IRR at 88.2%. This demonstrates that CA can provide a better self-healing function even if the cracks appear at a late age, but its effectiveness diminishes with the increasing cracking ages. This is mainly due to the relatively high hydration degree when the cracking age is late, and there are fewer unhydrated phases around the crack. In addition, mortars at a late cracking age have less free Ca^{2+}, so fewer healing products can be generated, resulting in poorer crack healing, and thus exhibiting a poorer gas impermeability compared to mortars at earlier cracking ages.

3.2.4. *Water absorption test*

The CWAs of PACAs at different cracking ages before and after healing are shown in Figure 8. The total CWAs of all specimens increase rapidly with time, with a faster increase in the early stage and a gradual slowdown in the late stage. For the PACAs before healing, the specimen pre-cracked at 3 days has the highest total CWA, and the total CWA of the specimen pre-cracked at 7 and 14 days are slightly lower than that of the specimen pre-cracked at 3 days. Furthermore, the total CWA of the 3-days PACA before healing is 1.6 times as high as that of the 28-day PACA before healing. More importantly, at the same cracking ages, the total CWAs of PACAs after healing are significantly lower than those of PACAs before healing. The reduction in the total CWAs of PACAs after healing indicates that the water impermeability of PACAs is recovered, so CA is beneficial to increase the water impermeability recovery of PACAs. Similar to the results for chloride ion permeability and gas permeability, the promotion of the self-healing behavior by CA decreases as the cracking age increases. The total CWAs of the PACAs pre-cracked at 3, 7, 14, and 28 days after healing are 72.1, 64.8, 56.6, and 24.1% lower than that of PACAs before healing, respectively (Figure 8). Among the tested specimens, the PACA pre-cracked at 3 days after healing has the lowest total CWA. This may be due to the components in CA that can accelerate the formation of healing products when the cracking age is early. As $Ca(HOOC)_2$ in CA is readily soluble in water, its Ca^{2+} release upon dissolution in water increases the Ca^{2+} concentration in the pore solution at an early cracking age. Therefore, the relatively high concentration of free Ca^{2+} in mortar at the cracking age of 3 days, is more favorable for the formation of healing products. Moreover, the glycine in CA can chelate with the free Ca^{2+} to form an unstable chelate compounds (calcium glycinate). As water penetrates inside the matrix, calcium glycinate dissolves and releases some Ca^{2+} in a relatively limited space [36]. This indirectly increases the Ca^{2+} concentration and accelerates the reaction of Ca^{2+} and SiO_3^{2-}, which accelerates the formation of healing products. The formation of a large amount of healing products promotes the cracks closure and thus recovers the water impermeability of PACAs. However, among all the specimens after healing, the specimen pre-cracked at 28 days after healing has the lowest total CWA. When the cracking age is late, the content of free Ca^{2+} in the pore solution is very low, which produces a limited amount of healing products. Therefore, the water impermeability of the specimen at a late cracking age cannot be recovered as well as that of the specimen at an early cracking age, even if these two specimens are at the same healing age.

The sorptivity coefficients based on a linear fit of the statistical data in Figure 8 are shown in Figure 9. The specimen pre-cracked at 3 days before healing has the highest sorptivity coefficient, but the specimen after healing has the lowest sorptivity coefficient. Compared to the specimens before healing, the specimens pre-cracked at 3, 7, 14, and 28 days show a reduction in sorptivity coefficient by 72.1, 65.9, 58.3, and 38.4% after healing, respectively. The reduction in sorptivity coefficient provides evidence of the pores or cracks filling and sealing, which also confirms that CA promotes the closure of cracks and enhances the microstructure, thereby increasing the water impermeability of mortar. Among all the PACAs after healing, the lowest sorptivity coefficient is observed for the specimen pre-cracked at 28 days. It is known that the water impermeability of mortar is not only related to the internal pore structure but is also influenced by cracks. When the cracks occur at a late stage, the matrix cannot provide sufficient Ca^{2+} for self-healing process due to the low content of unreacted phases [13]. More importantly, the internal microstructure of the matrix at a late age is denser, which makes water penetration more difficult. Based on this, the unstable metal chelate compounds formed by calcium ion chelators (TEA and glycine) and Ca^{2+} have difficulty dissolving and releasing Ca^{2+} under water-deficient conditions, which hinders the self-healing process. To summarize, the self-healing behaviors of CA-containing mortars at different cracking ages is significantly affected by the process of healing products formation at cracks, and the further explanation can be seen in Figure S2.

3.3. *Influence of external conditions on self-healing behavior of mortar containing CA*

3.3.1. *Compressive strength*

The compressive strengths of PACAs exposed to different external conditions at different exposure ages are shown in Figure 10. With the increase of exposure ages, the compressive strengths of the PACAs exposed in the four types of external conditions all gradually increase. Moreover, for specimens exposed in same conditions, the growth speed of compressive strength is faster in the first 14 days, while it gradually becomes slower from 14 to 56 days. This is due to the low hydration degree of cement, sufficient water, and enough available space for products generation in the early exposure stage (before 14 days), the penetration and the complexation-precipitation reaction of

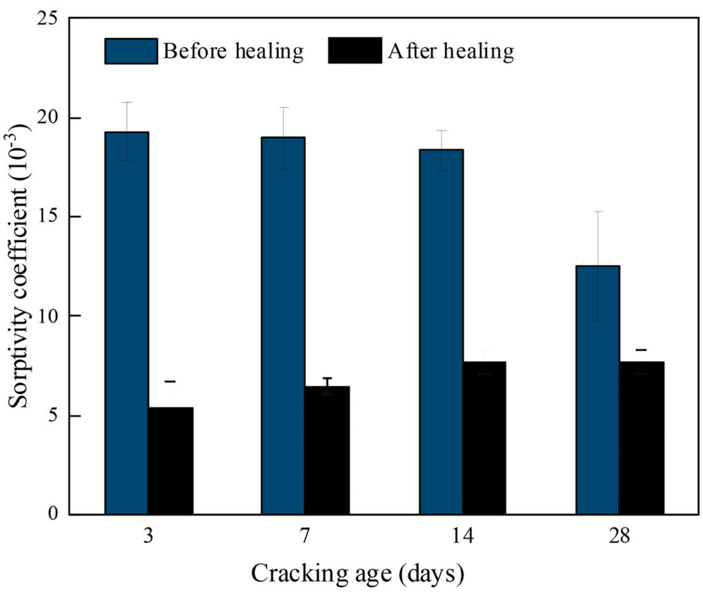

Figure 9. Sorptivity coefficients of PACAs at different cracking ages before and after healing.

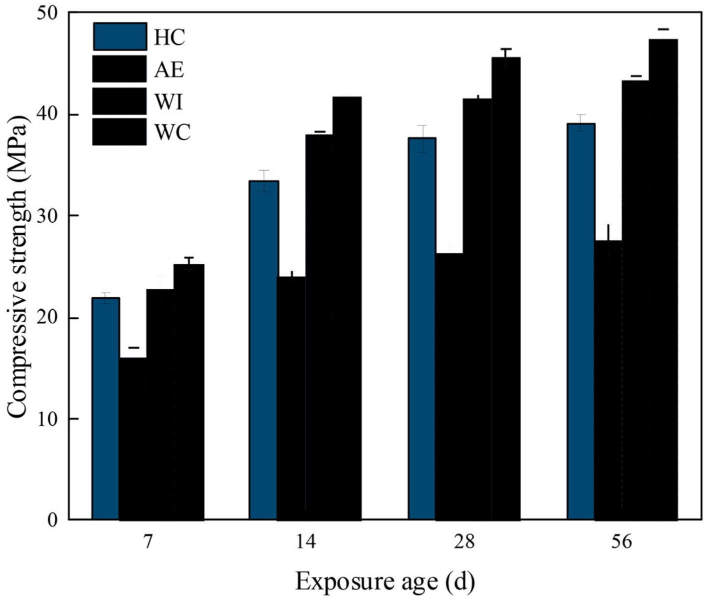

Figure 10. Compressive strengths of PACAs exposed to different external conditions.

active chemicals assist each other and jointly contribute to the recovery of mechanical properties [16]. Besides, NS can also accelerate the cement hydration and enhance the mechanical properties of mortar [42], this is because NS plays a nucleation role at the early stage and promotes the early crystalline nucleation of cement hydration products . Moreover, there is a synergistic effect of glycine and TEA on cement hydration, which greatly promotes the hydration of tricalcium aluminate based on complexation and transport of metal cations [43] . TEA can slow down the consumption of glycine at the early stage of cement hydration and prolong its action duration [33]. In contrast, the hydration degree is relatively high for mortars at 28 and 56 days, the matrix is denser and the impermeability becomes higher. Due to the depletion of CA, the penetration and complexation-precipitation reaction of active chemicals are gradually reduced, thus the speed of strength recovery becomes slower.

Regarding the PACA exposed to HC condition as a control group, the PACA under AE condition exhibits the lowest compressive strength at the exposure age of 7, 14, 28, and 56 days, which are 26.9, 28.1, 30.3, and 30.0% lower than HC conditions, respectively. This may be due to the low humidity in the air, which requires water involvement for the formation of healing products. In the condition of water deficiency, the hydration of unhydrated phases, carbonation of hydrated phases, and penetration of active chemicals are hard. The compressive strengths of PACAs under WI condition are 22.8, 37.9, 41.6, and 43.2 MPa at the exposure age of 7, 14, 28, and 56 days, which are 4.1, 13.5, 10.6, and 10.3% higher than HC condition, respectively. This is because WI condition can provide adequate liquid water for self-healing process [4]. However, the PACA exposed to WC condition has the highest compressive strength at any exposure age. This is because, in WI condition, prolonged water immersion reduces the ion concentration in pore solution and may be detrimental to healing products reaching supersaturation and precipitation. The specimens under WI condition have a high internal moisture content and excessive water, the excessive water decreases the surface energy of the hydrated products and the van der Waals bonding among the hydrated products [36]. For specimens in WC condition, the water soaking process provides water and the active chemicals can be dissolved, the drying process allows the excess water to evaporate, indirectly increasing the Ca^{2+} concentration in pore solution and promoting the formation of more healing products. In contrast to WI condition, WC condition prevents the loss of CA and reaction products from the mortar with cracks during the healing process; in contrast to the AE condition, WC condition provides water for the self-healing environment of mortar. Furthermore, compared to other conditions, WC condition allows the products formed during the healing process to be trapped at certain locations of the specimen. Last, repeated soaking and drying cycles form denser healing products. In a word, these four external conditions have a healing effect on the compressive strength of mortar, and the compressive strength enhancement after healing is in the order of WC > WI > HC > AE.

3.3.2. Chloride ion permeability

The CPCs of PACAs exposed to different external conditions are shown in Figure 11. It is consistent with the recovery trend of the compressive strengths (Figure 10), the CPCs of PACAs under the four external conditions gradually decrease with the increase of exposure ages. Its change speed is faster in the early stage (before 14 days) and gradually becomes slower in the later stage (28–56 days). At all exposure ages in the test, the PACAs under AE, HC, and WC conditions show poorer chloride ion impermeability than that under WI conditions. When exposed for 7 days, the CPCs of PACAs under WI condition are 11.7, 28.0, and 5.6% lower than those of PACAs under HC, AE, and WC conditions, respectively. When

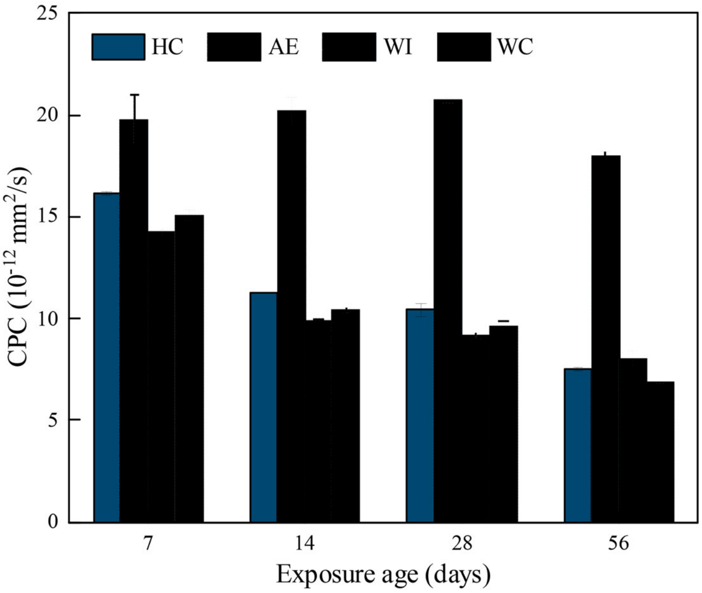

Figure 11. CPCs of PACAs exposed to different external conditions.

exposed for 28 days, the CPCs of PACAs under WI condition are 12.3, 55.9, and 5.5% lower than those of PACAs under HC, AE, and WC conditions, respectively. The reason is that in the early healing stage, the cement hydration and the penetration-crystallization of CA are mostly influenced by environment humidity. Adequate water contact with cracks promotes the dissolution of active chemicals, hydration of unhydrated phases, and carbonation of hydrated phases. In the early exposure stage, the PACAs under WC conditions with direct water immersion exhibit a more substantial enhancement of chloride ion impermeability, compared to the PACAs under other conditions. It leads to a conclusion that the CPCs of PACAs under WI condition at the exposure age of 7, 14, and 28 days are all the smallest of the four conditions, and the further mechanistic elaboration is shown in Figure S3.

Furthermore, for all the PACAs under the four conditions, the chloride ion impermeability at the exposure age of 7, 14, and 28 days is in the order of WI > WC > HC > AE, but the chloride ion impermeability at the exposure age of 56 days is in the order of WC > HC > WI > AE. This means that the CPC of PACA under WI condition is only lower than that of PACA under AE condition at the exposure age of 56 days. This is because of the higher hydration degree and denser microstructure of the matrix at 56 days, the self-healing process in the late healing stage is dominated by the active chemicals in CA. Besides, the prolonged water immersion results in lower alkalinity at cracks and in pore solution, accompanied by the continuous dissolution of Ca^{2+}. However, the PACA under HC condition cannot come into direct contact with water compared with the PACA under WI condition, so Ca^{2+} dissolving from the matrix under HC condition is less severe than that under WI condition. Moreover, properly increasing the alkalinity of environment is beneficial to the formation of healing products such as $CaCO_3$ [35]. Therefore, at the exposure age of 56 days, the CPC of PACA under HC condition is lower than that of PACA under WI condition.

It is also found that at different exposure ages, the exposure condition that makes the specimen the lowest CPC is different. When the exposure age is within 28 days, the CPC of the PACA under WC condition is not the lowest. But when the exposure age reaches 56 days, the PACA under WC condition has the lowest CPC, which is 62.0, 9.5, and 15.1% lower than those of PACAs under AE, HC, and WI conditions, respectively. To further analyze the self-healing behavior of PACAs under WC condition, the excess water can evaporate during the drying process and thus the ion concentration at the crack increases. In this case, the content of reactants used for further reactions is relatively high and the water content is sufficient for the permeation process [31]. Besides, CO_2 penetrates the matrix and dissolves in pore solution during the drying process with a certain humidity, leading to the formation of added carbonates that contribute to crack healing. In a word, it is suggested that the WC conditions can facilitate the interaction of water, CO_2, and unhydrated phases [44]. Moreover, the PACA under AE condition has the largest CPC at all exposure ages. It is mainly due to the lack of water, whereas sufficient moisture is an essential requirement for crack healing. In addition, the CPC of PACA under AE conditions decreases with increasing exposure age up to 28 d. Hu et al. [16] claimed that when the ambient humidity was low, the specimen is prone to dry shrinkage. This may be because the drying shrinkage of mortar is very intense within 28 days of exposure, severe drying shrinkage makes the initial cracks further expand or even appear interconnected cracks. Ultimately, this leads to a reduction in the chloride ion impermeability of mortar. In contrast, when exposure age reaches 56 days, the drying shrinkage slows down, and the filling of pores and cracks by the formed healing products enhances the chloride ion impermeability of mortar.

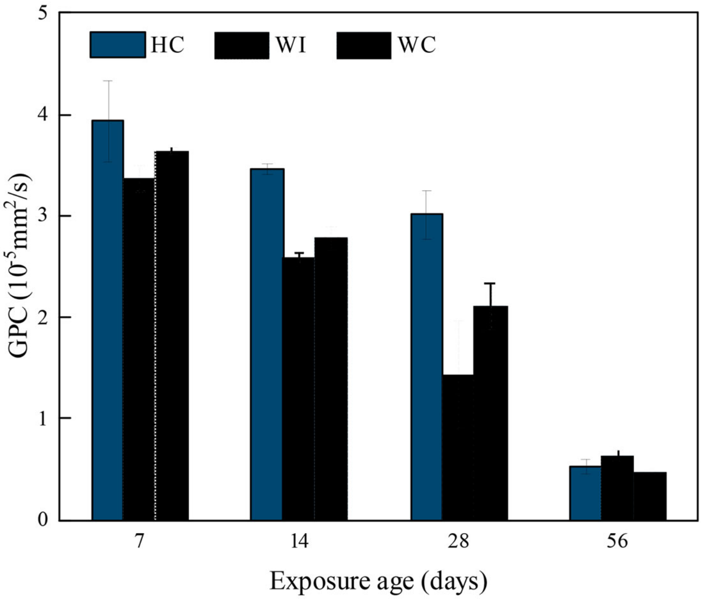

Figure 12. GPCs of PACAs exposed to different external conditions.

3.3.3. Gas permeability

The GPCs of PACAs exposed to different external conditions are shown in Figure 12. In this test, the GPCs of PACAs exposed to AE condition are not presented, since they are not in the same order of magnitude as the results of PACAs exposed in HC, WI, and WC conditions. The GPCs of PACAs exposed to HC, WI, and WC conditions all increase with the increasing exposure ages, and the specimens exposed for 56 d have the lowest GPC compared to other exposure ages. Meanwhile, the difference in the GPCs of PACAs under different exposure conditions becomes greater with the increasing exposure ages, and this may be related to the various self-healing efficiency of CA-containing mortars under different exposure conditions. The PACA under WI condition exhibits the optimum healing performance when the exposure age is within 28 days, follows by the PACA under WC condition, and finally the PACA under HC condition. When exposed for 7 days, the GPC of PACA under WI condition is 14.3 and 7.4% lower than those of PACAs under HC and WC conditions, respectively. When exposed for 28 d, the GPC of PACA under WI condition being 52.4 and 31.9% lower than those of PACAs under HC and WC conditions. It means that, for PACAs within 28 d of exposure, direct water contact is more favorable for the rapid reduction in GPCs. The reason is that the enough water content is essential to the continuous hydration of unhydrated phases, the osmotic crystallization of the active chemicals, and the carbonation of CH, and WI condition is available to provide a large amount of water.

When exposed for 56 days, the PACA under WI condition exhibits the highest GPC at 0.634×10^{-5} mm^2/s, which is 21.5 and 35.3% higher than those of PACAs under HC and WC conditions, respectively. During the exposure process, WI condition causes further dissolution of Ca^{2+} from cement hydrates and facilitates the healing products generation, but the healing products are loose and easily dissolved in the soaking water. The healing products at the cracks of PACAs under HC and WC conditions are denser, resulting in a lower GPC.

3.3.4. Water absorption test

The CWAs of PACAs exposed to different external conditions are shown in Figure 13. The total CWAs of PACAs under the four conditions all decrease with the increasing exposure ages, and it demonstrates that CA is effective in producing self-healing products to heal cracks under the four conditions. Obviously, the total CWA of PACA under AE condition is the largest at all the exposure ages, but the total CWA of PACA under AE condition still decreases with the increasing exposure ages. It demonstrates that the water impermeability of PACA under AE condition also recovers within a certain exposure period, and the cracks fill with self-healing products. For the specimens under the four conditions, when exposed for 7, 14, and 28 days, the total CWA of PACA under WI condition is the lowest. It implies that the closure behavior of cracks inside mortar under WI condition is optimum within 28 days, and the self-healing products refine the pores and filled the cracks, which results in a relatively low total CWA. In the early exposure stages (7–28 days), WI condition can increase the probability of direct contact between the exposed unreacted phases and water, and it allows for a rapid formation of healing products and makes a rapid reduction of the total CWA of the specimen. Moreover, the total CWA of PACA under WI condition at the exposure age of 56 days is lower than that of PACA under WI condition at the exposure age of 28 days. However, when exposed for 56 days, the total CWA of PACA under WI condition is 1.2 and 2.3 times as high as those of PACAs under HC and WC conditions (Figure 13(d)). It indicates that CA still leads to the decreasing of cracks in PACAs under WI condition when the exposure age is relatively late. However, in CA-containing mortar, the self-healing products may be easily to be washed away by permeated water [13], and prolonged immersion

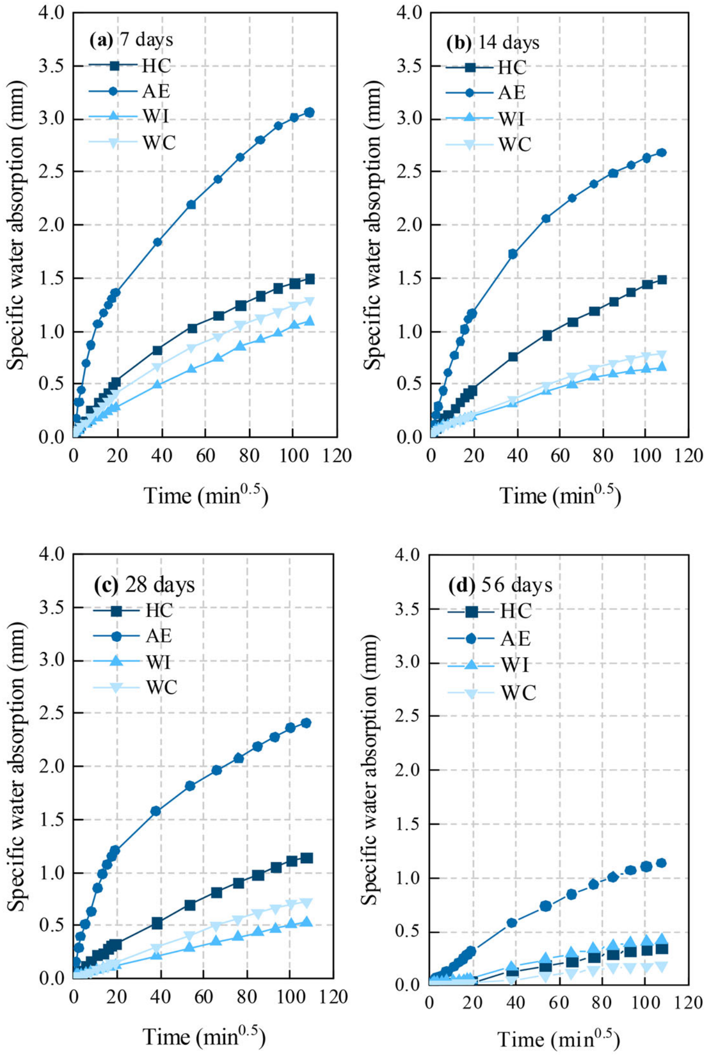

Figure 13. CWAs of PACAs exposed to different external conditions at different exposure ages, the specimen exposed for 7 days (a), 14 days (b), 28 days (c), and 56 days (d).

may affect the stability of healing products and the compactness of the healed matrix [36]. Thus, when exposed for 56 days, the total CWA of PACA under WI condition is only lower than that of PACA under AE condition.

3.3.5. *Crack healing behavior*

To understand the influence of exposure conditions on the crack healing behavior of PACA, forty specimens were exposed to the four conditions, and the remaining CW was tracked and recorded during the exposure process. Figure 14 shows the statistics of the CWs of PACAs exposed to the four conditions after exposure for 7, 14, 28, and 56 days, respectively. As the exposure age increases, the surface cracks in the four conditions tend to close, but their CWs decrease to different levels. When exposed for 7 days, the average CWs of PACAs under HC, AE, WI, and WC conditions decrease to 162, 190, 150, and 133 μm, respectively (Figure 14(a)). When exposed for 14 days, the average CWs of PACAs under HC, AE, WI, and WC conditions decrease to 124, 177, 138, and 88 μm, respectively (Figure 14(b)). It indicates that during the early stages of healing (7–14 days), the average CWs of PACAs under WC condition are the smallest compared to the PACAs under other conditions, and the healing products formed are the most effective in filling surface cracks. When exposed for 28 days, the average CWs of PACAs exposed to HC, AE, WI, and WC conditions are reduced by 69.0, 27.2, 74.1, and 85.3%, respectively, compared to the initial CW (Figure 14(c)). When the exposure age reaches 56 days, the average CWs of PACAs exposed to HC, AE, WI, and WC conditions decrease by 83.5, 32.2, 78.33, and 93.7%, respectively, compared to the initial CWs (Figure 14(d)). It proves that the self-healing of cracks appears rapidly in the early stages of exposure (before 28 d), and the average CWs of PACAs are still reduced to some extent by exposure for 56 days. Moreover, after exposure for 56 days, the average CWs of PACAs under HC, AE, WI, and WC conditions are reduced by 46.9, 6.9, 16.2, and 56.8%, respectively, compared to those of PACAs exposed for 28 days (Figure 14(c,d)). It demonstrates that when the exposure age increases from 28 to 56 days, the CWs of PACAs under different conditions continue to decrease. More importantly, the PACA under WC condition consistently has the lowest average CW at all exposure ages, which implies that the PACA under WC condition has the optimum

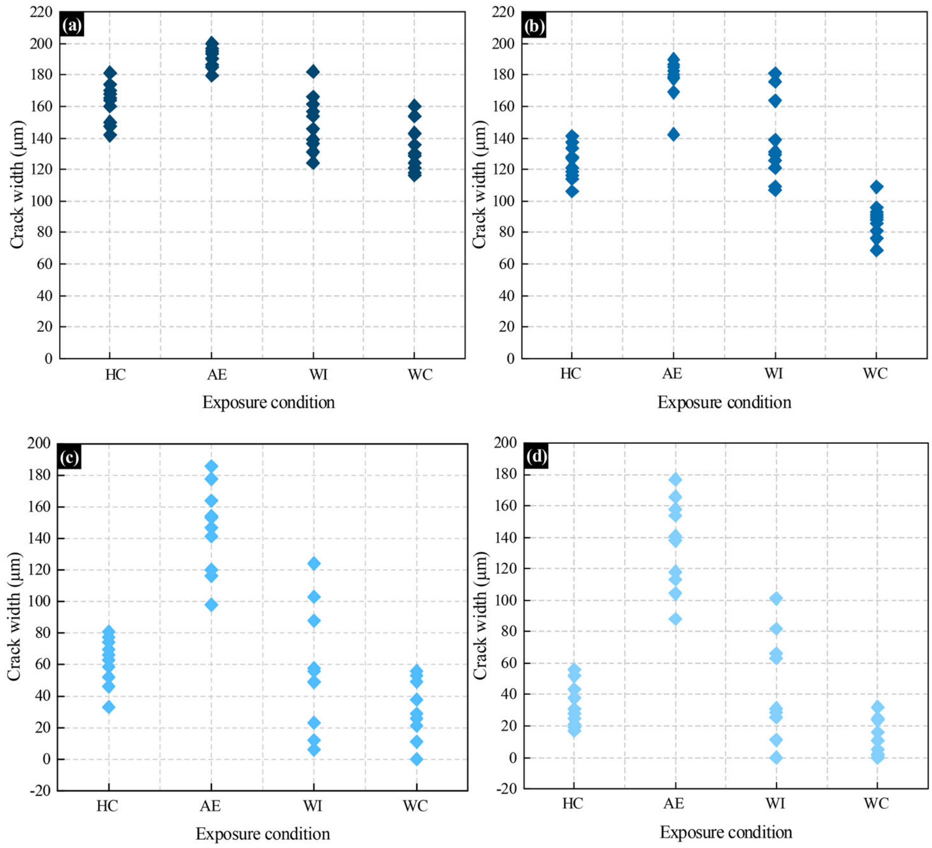

Figure 14. Apparent CWs of PACAs exposed to different external conditions at different exposure ages, (a) 7 days, (b) 14 days, (c) 28 days, and (d) 56 days.

crack healing behavior compared to other conditions. This may be one of the important factors for PACAs under WC conditions to show the best strength and impermeability recovery, and the related explanation can be seen in Figure S3.

3.3.6. SEM analysis

To investigate the influence of external conditions on the self-healing behavior of CA-containing mortar, the cracks morphology of PACAs exposed to different external conditions for 28 d are characterized by SEM in Figure 15. As shown in Figure 15(a), some of the pores are filled by the healing products, which seem to generate crystalline products with larger size but still less than 2 μm. The formation of healing products dominated by C–S–H gels and $CaCO_3$ is observed in the sample exposed to HC condition, mainly due to the dissolving and re-deposition of Ca^{2+}, diffusion of unhydrated phases, and CO_3^{2-} into cracks [7,35]. As shown in Figure 15(b), CH can be observed in the middle of the left panel, while the right panel shows that only a small amount of C–S–H gel is present at the crack of the sample exposed to AE condition. This implies that the sample under AE condition has a lower hydration degree and a coarser pore structure than the samples under other conditions. This is due to the low humidity in AE condition: the absence of moisture hinders the hydration reaction of unhydrated phases. Comparing to Figure 15(a,b), the surface of the sample under WI condition undergoes a very distinct change, with clusters of large-sized granular crystals covering the surface (Figure 15(c)). It may be attributed to the dissolution of Ca^{2+} from the hydration products exacerbated by the soaking water. The production of lamellar crystals is observed, and there are loose C–S–H gels attached to the crystals. However, these healing products formed do not seem to fill the pores effectively. Moreover, more crystals with small particle sizes are formed in the sample exposed to WC condition, and the C–S–H gels present among the crystal particles seems to be dense (Figure 15(d)). It proves that the pore of the sample is filled due to the growth and stacking of small particle crystals. Moreover, the $CaCO_3$ formed in the samples in different environments differs significantly, with Figure 15(a) being a well-crystallized $CaCO_3$, Figure 15(c) having a layered type of $CaCO_3$ and Figure 15(d) having a spherical type of $CaCO_3$.

It is found that CA does not seem to affect the types of healing products, but the external conditions significantly influence the compactness, morphology, and distribution of the healing products. Besides, it can be inferred that the reductions in the CWs of surface cracks are caused by the formation of crystals and hydration products, and the healing degrees of cracks are more closely related to the content of healing products. This leads to different degrees of strength and impermeability recovery of PACAs exposed to different external conditions.

3.3.7. Pore structure analysis

The 3-day pre-cracked pastes containing CA after exposure in different external conditions for 28 days

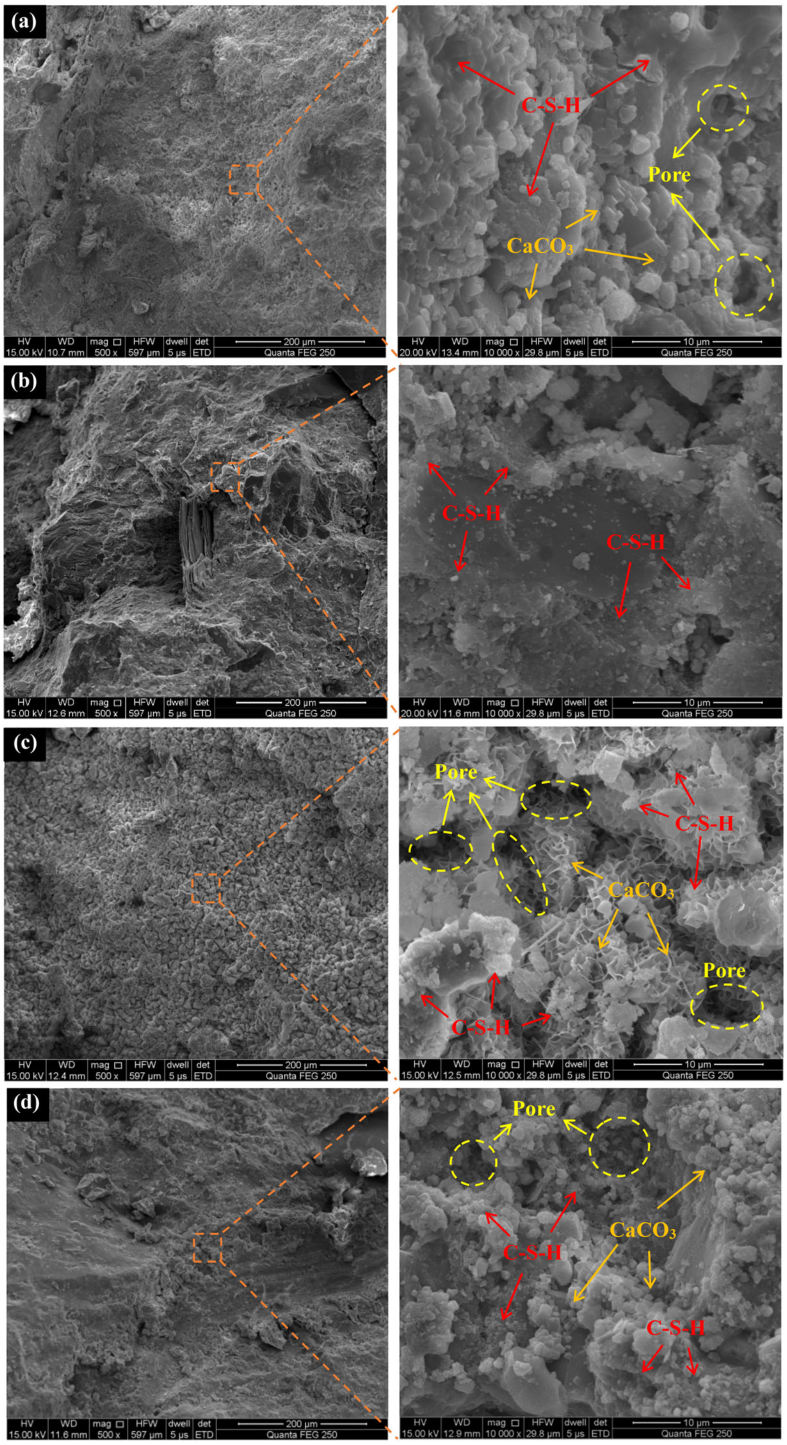

Figure 15. SEM images of the cracks of PACAs exposed to (a) HC, (b) AE, (c) WI, and (d) WC conditions for 28 days.

were sampled and then analyzed using MIP (Figure 16). The sample named as 'Unhealed' is the 3-day pre-cracked paste without exposure process. Comparing to the unhealed sample, the cumulative pore volume of the samples exposed to the four conditions all decreases (Figure 16(a)). The cumulative pore volume of the samples exposed to HC, AE, WI, and WC conditions is 0.0729, 0.0755, 0.0715, and 0.0624 mL/g, respectively, which is 3.80, 0.37, 5.65, and 17.66% lower than that of the unhealed sample. It is also found that after exposure for 28 days, the sample under WC condition exhibits the lowest porosity. However, the corresponding permeability results show that the PACA under WI condition has the lowest permeability coefficient. Though porosity and permeability are positively correlated, higher porosity cannot necessarily mean lower permeability [45]. The size, interconnectivity, and shape of pores all affect the transport properties of water and various ions, and the healing behavior of cracks also have a great effect on the permeability of self-healing mortar.

To further investigate the effect of pore size distribution, the pore sizes of cement paste are divided into four ranges: harmless pores (<20 nm), less harmful pores (20–

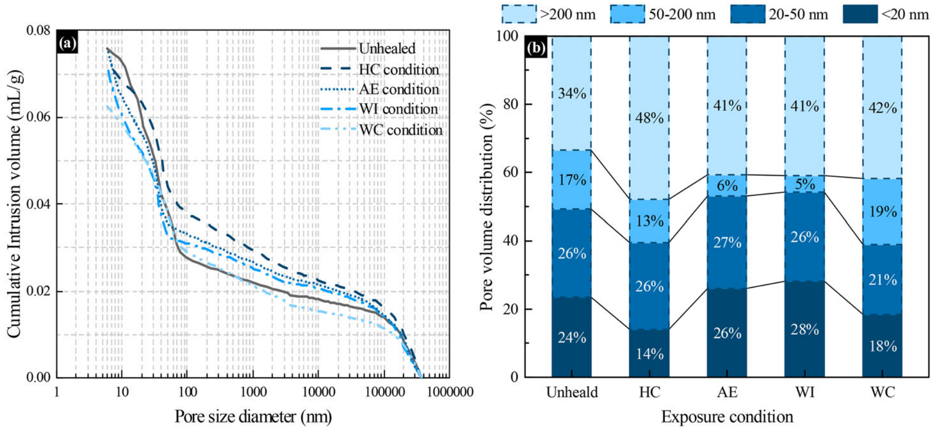

Figure 16. Pore structure of pre-cracked paste containing CA exposed to different external conditions for 28 days, (a) cumulative pore volume, and (b) pore volume distribution.

50 nm), harmful pores (50–200 nm), and very-harmful pores (>200 nm). The pore volumes corresponding to the above pore sizes are normalized to facilitate a comparison of the influence of different external conditions on the pore structure of paste containing CA (Figure 16(b)). Compared to the unhealed sample, the sample exposed to AE condition shows a tendency to conversion of harmful pores to harmless and less harmful pores. It indicates that the paste containing CA exposed to a low humidity condition can still refine the pore structure and heal cracks. It is generally believed that capillary pores in the size range of 5–50 nm can generate large capillary shrinkage forces that cause shrinkage of mortar [7,44]. It seems to be more likely to produce much-harmful pores in the sample exposed to AE condition, which may be due to the compression of gel pores caused by the evaporation of internal water. It not only intensifies the deterioration of the initial cracks and pores, but also exacerbates the transformation of some of the harmful pores into much-harmful ones. Among the samples under the four conditions, the sample exposed to WI condition has the highest percentage of harmless pores and the lowest sum of the percentages of much-harmful and harmful pores. It seems to lead to a conclusion that direct water exposure can increase the percentage of harmless and less harmful pores, and optimize the pore distribution, thus affecting the permeability of the self-healing sample. Moreover, the average pore size of the unhealed sample, and the samples under HC, WI and WC conditions are 22.66, 12.12, 15.28, 10.33 nm, respectively. This indicates that the HC, WI, and WC conditions are beneficial in refining the pores of CA-containing samples.

3.4. Comparison of the properties of multiple self-healing components

To confer superior self-healing capability to CBM, SCMs, bacteria, and capsules are introduced into CBMs as self-healing components (46–49) . Figure 17 illustrates the relative crack healing ratios of CBMs containing different self-healing components with different initial CWs and the increments of 28-day compressive strengths of CBMs containing different self-healing components, compared to the samples without self-healing components. As shown in Figure 17(a), ground granulated blast furnace slag (GGBS) was more effective as a self-healing stimulator for the specimens with initial CWs up to 0.2 mm, and its relative crack healing ratio decreased with increasing GGBS content. In the initial CW range of 0.05–0.45 mm, the CW of the specimen with bacteria was reduced to varying degrees after healing, and the relative crack healing ratios increased with the increasing initial CWs, suggesting that bacteria were more efficient in healing large-sized cracks. However, it is noteworthy that the relative crack healing ratios of CA-containing specimens appear to be higher than those of the specimens with bacteria, when the initial CW is in the range of 0.2–0.4 mm. Furthermore, it is also found that the relative crack healing ratios of the specimens with capsules decreased with the increasing initial CWs, implying that the self-healing efficiency of specimens with capsules decreased as the initial CWs increased.

The relative crack healing ratio is determined by the ratio of the width change of surface crack before and after healing in the CBMs with self-healing component to the width change of surface crack before and after healing in the CBMs without self-healing component. The relative crack healing ratio can be calculated as Equation (3).

$$\text{Relative crack healing ratio} = \frac{W'_b - W'_a}{W_b - W_a} \times 100\% \quad (3)$$

where, W'_b is the CW of specimen with self-healing component before healing (μm), W'_a is the CW of specimen with self-healing component after healing (μm), W_b is the CW of specimen without self-healing component before healing (μm), and W_a is the CW of specimen without self-healing component after healing (μm).

Nevertheless, the self-healing efficiency is only one aspect, the mechanical properties of CBMs mixed with different self-healing components and the cost-effectiveness of the self-healing components also need to be considered. As shown in Figure 17(b), CA addition increases the 28-day strength of the specimen by 35.8%, and the addition of 30 and 60% GGBS increased the 28-day strength of the specimen by 5.1 and 12.2%, respectively.

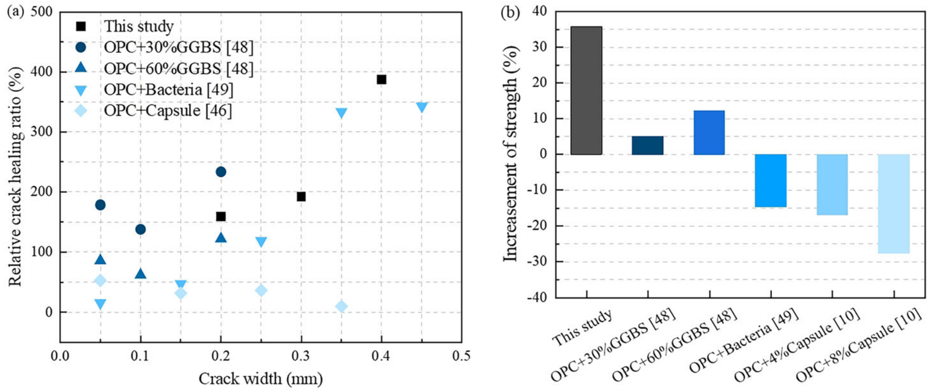

Figure 17. Comparison of CBMs containing multiple self-healing components, (a) relative crack healing ratios, and (b) increments of 28-d compressive strengths.

However, bacteria addition decreased the 28-day strength of the specimen by 14.5%. As the study by Feng et al. [46] did not show the compressive strength of the specimen with capsules, but a study by Dong et al. [10] showed that the capsules with the particle size of 230 μm was detrimental to the 28-day compressive strength of specimen. Besides, the specimen with capsule had a lower 28-day compressive strength as the capsule content increased [10]. In addition, the high cost of capsules also limits its application.

4. Conclusions

The influence of crack widths (CWs), cracking ages, and external conditions on the self-healing behavior of mortar containing a self-developed crystalline admixture (CA) are investigated. Based on the results obtained in this study, the following conclusions can be drawn.

1. The self-healing capability of CA-containing mortar was much higher than that of the plain mortar, regardless of the set initial CWs, cracking ages, and external conditions, indicating that CA could effectively enhance the self-healing capability of mortar. When the initial CW was 0.3 mm, the average CW of CA-containing mortar after healing for 28 days was reduced by 72.5% compared to that of plain mortar.
2. Although the self-healing efficiency of CA-containing mortar decreased as the initial CW increased, CA was able to effectively close cracks up to 0.3 mm in width. In addition to the self-healing behavior of surface cracks, CA also had a good contribution to the self-healing of the matrix. When the initial crack width was 0.2 mm, the sorptivity coefficient of CA-containing mortar after healing for 28 days was reduced by 75.4% compared to that of the plain mortar after healing for 28 days.
3. The recovery ratios of strength and impermeability of CA-containing mortar decreased with the increasing cracking age. Although the self-healing efficiency of CA-containing mortar was higher at an early cracking age, CA could still promote the recovery of strength and impermeability for mortar at a late cracking age. The compressive strength of CA-containing mortar with cracks prepared at 56 days after healing can be kept at 49.2 MPa.
4. Different external environments produced different self-healing behavior. Water immersion (WI) condition was more beneficial for the recovery of strength and impermeability of CA-containing mortar, as the exposure age did not exceed 28 days. As the exposure age reached 56 days, wet-dry cycles (WC) condition was more beneficial for the recovery of strength and impermeability of CA-containing mortar.
5. Water is a key factor in the property recovery of mortar, and mercury intrusion porosimetry (MIP) analysis indicated that the sample under the AE condition had a higher porosity compared to other conditions. Scanning electron microscopy (SEM) analysis indicated the healing process mainly produced $CaCO_3$ and C-S-H gels, with fewer healing products produced under AE conditions and more healing products produced under WI and WC conditions.

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