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Self-healing performance of cement mortar mixed with pulverized clinker and inorganic admixture

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Abstract. This study evaluated the mechanical properties and self-healing performance of cement mortar containing pulverized clinker, calcium sulfoaluminate (CSA), and Na_2SO_4. Mechanical properties of cement mortar were investigated by measuring compressive strength, and sealing efficiency were evaluated by a hydrostatic permeability test and a nitrogen gas diffusion test. Moreover, the healing products adhering to the cracks were visually observed with an optical microscope and a scanning electron microscope (SEM). As a result, incorporating pulverized clinker with mineral admixtures increased the 3- and 28-day strength by approximately 20%. There was a difference in the sealing efficiency depending on the evaluation method. The sealing efficiency of the gas diffusion test was underestimated due to the difference in characteristics according to the type of medium passing through the crack. Nevertheless, when the inorganic additive was mixed with cement mortar, $CaCO_3$ precipitated as the healing product within 0.3 mm cracks and improved self-healing performance.

1 Introduction

Infrastructure and buildings experience degradation due to aging, environmental erosion, and natural or artificial hazards. Structural condition assessments and maintenance processes are receiving worldwide attention [1]. As the proportion of aging infrastructure and buildings increases over time, maintenance costs are also expected to increase [2] steadily. In Korea, 17.3% of social infrastructures are over 30 years old, and 27.9% of facilities are 20 to 30 years old, and aging infrastructure is expected to increase within the next ten years rapidly. In particular, concrete structures older than 30 years require active performance improvement rather than periodic repair and reinforcement, and for this purpose, pre-emptive measures and technological advancement are needed.

Since concrete, universally applied to facilities such as buildings, bridges, and tunnels, has low tensile strength, it can cause shrinkage cracks during construction and cracks caused by external loads. In particular, microcracks in concrete can cause structural safety problems by promoting the movement of moisture and harmful ions, and oxygen to corrode the reinforcing bars inside the concrete [4, 5]. Since microcracks in concrete structures occur in hard-to-access areas and are difficult to visually identify, self-healing concrete techniques are needed to repair cracks naturally without external maintenance.

Self-healing concrete technology aims to close cracks after forming by adding various healing materials inside the concrete [6, 7]. In particular, self-healing concrete technology using cement-based materials such as supplementary cementitious materials (SCMs), expansion materials, swelling agents, and crystalline admixtures (CAs) has recently attracted attention, given economic feasibility [8 – 10].

Cement clinker is a solid material produced in the manufacture of cement as an intermediary product. The clinker can be produced with the same quality, and it is easy to process into desired particles through grinding. Since the clinker binder starts to hydrate from the surface, only the surface reacts to moisture and remains unreacted. Therefore, the clinker binder atomized to 30 ~ 300 μm reduces the unreacted amount due to the hydration reaction starting from the surface.

Most of these inorganic materials (partially) react during the initial hydration process when mixed with concrete, so it is challenging to secure healing performance at the time of crack generation. Therefore, it is necessary to block contact with moisture and secure unreacted particles through a surface coating of inorganic materials [11, 12]. Palmitic acid, saturated fatty acid, is an organic compound with a carbon chain structure, with good heat storage performance. So it is mainly used as a phase change material in construction materials. [13, 14]. When the cement-based healing material is coated with palmitic acid, the initial hydration reaction is expected to be delayed due to the water-repellent surface of the methyl group, and effective healing performance can be secured as the palmitic acid disappears after a certain period of time. In particular, compared to granular manufacturing of healing materials and encapsulation using organic/inorganic materials, input materials are economical, and the manufacturing method is simple.

Therefore, this study evaluated cement mortar's mechanical properties and self-healing performance using palmitic acid-coated pulverized clinker, CSA, and Na_2SO_4 as cement-based healing materials. The compressive strength was measured to assess the mechanical properties, and the constant water head permeability test and gas diffusion test were performed to evaluate the healing performance. In addition, the presence of the healing product precipitation, the change in crack width through an optical microscope, and the shape of the healing product through a scanning electron microscope (SEM) were observed.

2 Materials and Test methods

2.1 Materials

CEM I 52.5 N (Holcim, Belgium) was the main material (ordinary Portland cement, OPC). A pulverized clinker (PC, Hanil Hyundai Cement Co., South Korea), calcium sulfoaluminate (CSA, Denka CSA #20, Japan), and Na_2SO_4 (SAMCHUN, ≥ 99.0%, South Korea) were used as inorganic self-healing material (SHMs). Palmitic acid (SAMCHUN, ≥ 95.0 %, South Korea), an unsaturated fatty acid, was used as a coating material. The sand used to make the mortar had a particle range of 0-4 mm.

Fig. 1 indicates the particle size distribution of the raw materials. and the average particle sizes (D_{50}) of OPC, PC, CSA, and Na_2SO_4 were measured as 10.6 µm, 82.0 µm, 16.4 µm, and 256.7 µm, respectively. D_{50} of OPC and CSA were similar, and it was confirmed that most of the PC was within 300 µm. In the OPC and PC, CaO and SiO_2 accounted for more than 80%, and the SO_3 content in the PC was relatively small. CSA showed 56.5% CaO and 29.5% SO_3, presenting higher SO_3 content than OPC and PC.

For the coating of the SHMs, a 2% ethanol solution of palmitic acid was prepared and mixed with the SHMs, and then the ethanol was vaporized in a circulation chamber at 80 °C. It was confirmed that an organic compound presumed to be palmitic acid adheres to the surface of the inorganic particles produced by this coating method and contributes to water repellency. As shown in Fig. 2, water was dropped to check the water repellency according to the presence or absence of the coating on the PC, and the degree of absorption was visually observed. As a result, the uncoated PC absorbed moisture as soon as it came in contact with water, and the coated PC showed water repellency the moment it first came into contact with water and lasted for 24 hours.

Table 1 shows the mixing ratio of the mortar samples. RF-M is a reference sample made with OPC, and SH-M is a sample in which 15% of OPC is replaced with SHM. This SHM consisted of 10% PC, 2.5% CSA, and 2.5% Na_2SO_4. The water/binder ratio is 0.4, and the fine aggregate/binder is 2.0. After making samples, all samples were cured in a constant temperature of (20 ± 2) °C and a humidity chamber of relative humidity over 95% for up to 28 days.

To evaluate the mechanical properties of the self-healing mortar, three prism specimens of 40 mm × 40 mm × 160 mm were fabricated for each curing day. In the case of the constant water head permeability test and nitrogen gas diffusion test, six-disc specimens of ϕ100 mm × 50 mm were used for each test according to the KCI-CT114 [15] and Lee [16].

After curing for 28 days, a crack was generated in the disc specimens via an indirect tensile test. Then two 0.3 mm thick silicon sheets were inserted about 15 mm into both ends of the disc. The halves of the disc were placed back together with the silicon sheets in between, and everything was fixed with two clamps to control the crack width to about 0.3 mm. Crack length and width were measured using an optical microscope (DMC 2900, Leica, Switzerland) at the top and bottom of the specimen. For each crack, crack length was measured except for 15 mm of each end where the silicon sheets were inserted. The crack width was calculated at 12 points, 2 points per area, by dividing the crack section into three areas at the top and three areas at the bottom.

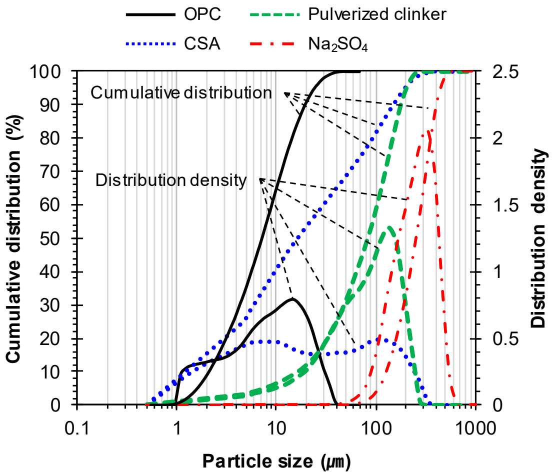

Fig. 1 Particle distribution of raw materials.

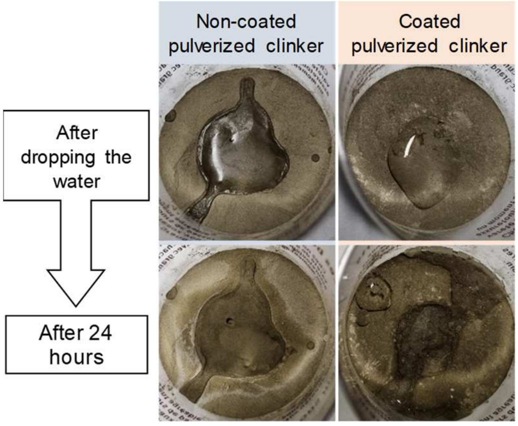

Fig. 2 Water repellency of coated pulverized clinker.

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

Label	Water	OPC	PC	CSA	Na_2SO_4	Sand
RF-M	40	100	-	-	-	200
SH-M	40	85	10	2.5	2.5	200

2.2 Test methods

2.2.1 Mechanical properties

The compressive strength was measured at 7, 14, and 28 days with a Walter + Bai AG machine (Switzerland) to evaluate the mechanical properties according to EN 196-1 [17].

2.2.2 Sealing efficiency

The constant water head permeability test using six ϕ100 mm × 50 mm disc specimens was conducted until the end of 28 days healing period (HP). As a healing condition, specimens with artificial cracks for evaluation of self-healing performance were immersed in water at a temperature of (20 ± 2) °C to the extent that the cracks were submerged and cured. Using the water permeability test device presented in KCI-CT114 [15], the flow rate per minute (mL/min) flowing from the head height of about 250 mm to the bottom of the disc was measured for 10 minutes through an electronic scale. Subsequently, the sealing efficiency was evaluated by calculating the water quantity per minute and crack length (mL/(min·mm)) and comparing the values after healing to the initial value [15].

The gas diffusion test proposed by Lee et al. [16] was also applied to evaluate the sealing efficiency. As in the constant water head permeability test, six-disc samples of the same size were separately manufactured and used. An oxide (O_2) gas sensor with 0.01% resolution was attached inside an acrylic cylindrical container with a volume of 500 ml with an inlet and outlet. After vacuum grease was applied to the top of the container to tightly adhere to the ϕ100 mm × 50 mm disc specimen, nitrogen (N_2) gas was injected into the container through the injection port. When the O_2 concentration in the vessel was stabilized, the inlet and outlet were closed simultaneously. The sealing efficiency was calculated by measuring the O_2 concentration that changes when O_2 in the air diffuses into the container through the cracks in the disk specimen.

At HP 28 days, the crack healing effect compared to the initial crack induction was visually observed through an optical microscope and SEM.

3 Test results and analysis

3.1 Mechanical properties

The compressive strength results are shown in Fig. 3. In the case of the RF-M sample, compressive strength was 49.9 MPa at seven days and 60.6 MPa at 28 days. The SH-M sample mixed with the SHM showed 58.8 MPa at seven days and 71.1 MPa at 28 days. From the results, the compressive strength of SH-M increased by about 17.3 to 17.8% compared to the RF-M.

Based on the strength results, it was found that the palmitic acid coating on the surface of the SHM had an insignificant effect on the strength development despite the delayed hydration reaction due to the initial water repellency. In addition, the use of PC-based inorganic self-healing mixtures was effective in enhancing strength. In particular, using CA and expansion materials containing sulfates such as CSA and Na_2SO_4 promoted ettringite formation during the initial hydration reaction, affecting the enhancement of initial strength.

The continuous strength improvement is likely due to the generation of C-S-H resulting from the additional hydration of C_3S and C_2S due to the palmitic acid-coating of the PC, which has a relatively larger particle size than OPC.

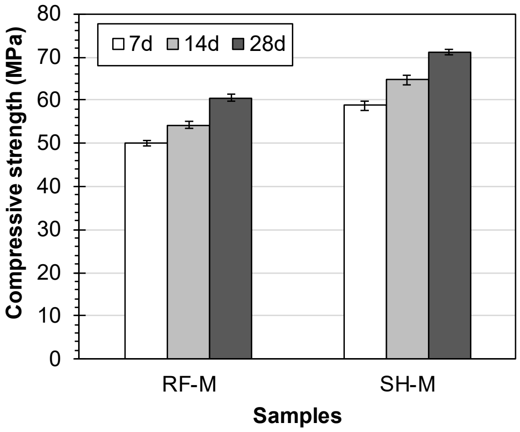

Fig. 3 Strength results of mortar samples.

3.2 Sealing efficiency

3.2.1 Constant water head permeability test

As a result of measuring the crack width for the specimen manufactured by targeting the crack width of 0.3 mm, the crack width was measured in the range of 0.291 to 0.301 mm. Fig. 4 shows the constant water head permeability test according to KCI-CT114 [15]. The sealing efficiency of RF-M was 21 – 49% at HP 7 days (△) and 50 – 65% at HP 28 days (▲). On the other hand, the sealing efficiency of SH-M was 48 – 63% at HP 7 days (○) and 72 – 84% at HP 28 days (●). From the test results, incorporating inorganic SHM improved the sealing efficiency by 30% on average at HP 28 days.

3.2.2 Gas diffusion test

Fig. 5 is the result of evaluating the healing efficiency by the gas diffusion test. The sealing efficiency tended to decrease as the initial crack width increased. The healing rate of RF-M was 11 – 44% at HP 7 days (△) and 37 – 51% at HP 28 days (▲), whereas that of SH-M was 18 – 40% at HP 7 days (○) and 46 – 55% at HP

28 days (●). The use of SHM increased sealing efficiency by 15% on average at HP 28 days.

The sealing efficiency results from the gas diffusion test were evaluated to be 32 – 41% lower than the constant water head permeability test result at HP 28-day

N$_2$ and O$_2$, used as the medium of the gas diffusion test, had a higher diffusion coefficient, lower friction coefficient, and viscosity coefficient than water, which was the medium of the constant water head permeability test. Therefore, when the N$_2$ passes through the crack, it seems that the reduction in the amount of runoff due to the precipitation of the healing product inside the crack is relatively small.

Through additional research in the future, it is necessary to consider the compatibility and equivalence of the sealing efficiency results obtained from both self-healing performance evaluation methods used in the current study.

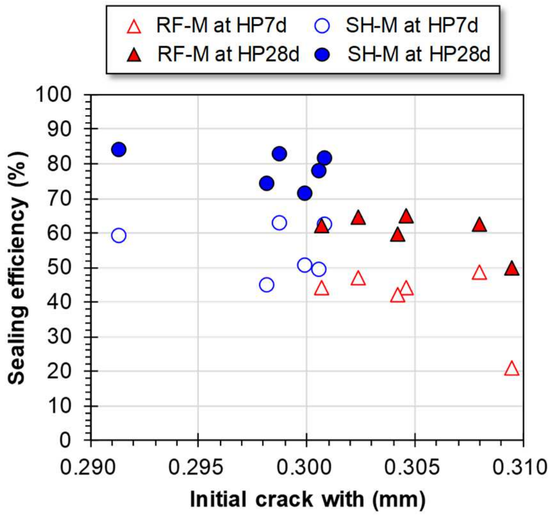

Fig. 4 Sealing efficiency results from constant water head permeability test.

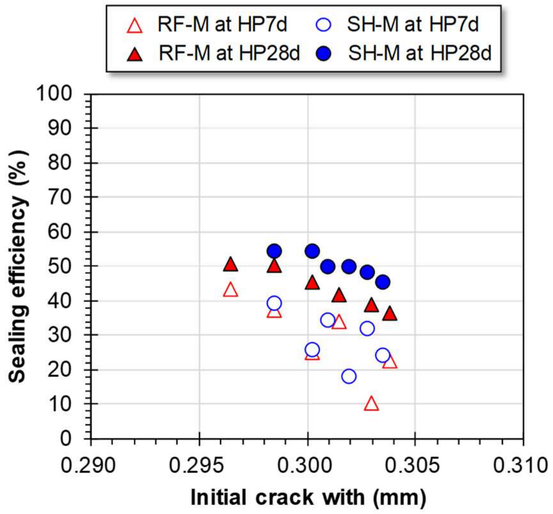

Fig. 5 Sealing efficiency results from gas diffusion test.

3.2.3 Observation of precipitation of sealing products

Fig. 6 shows the cracking of the SH-M sample at the time of crack induction and HP 28 days. At the time of crack induction, there was no precipitation of sealing products inside the crack. During the 28-day HP, white crystals precipitated on the surface of the crack and filled the inside of the crack, which is considered the main improvement in the sealing efficiency.

Sisomphon et al. [18] reported that when cement mortar containing CSA and CA was cured in water, calcium ions (Ca^{2+}) from the crack accelerated the precipitation of calcite (CaCO$_3$) on the surface of the crack and consequently contributed to the improvement of self-healing performance. The white crystals precipitated on the surface of cracks at HP 28 days were observed through SEM (Fig. 7), and these crystals in the form of a square or hexagonal columns were CaCO$_3$.

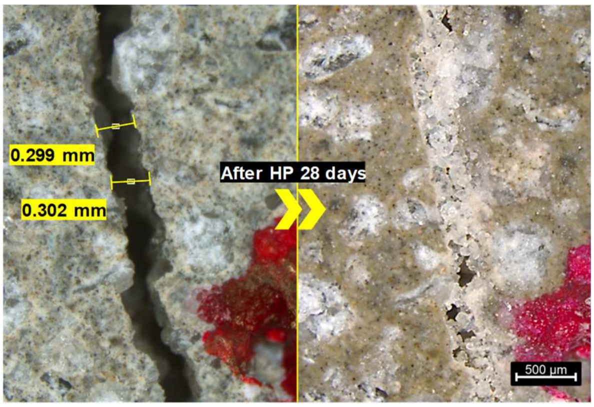

Fig. 6 Microscopic images of the crack in SH-M sample.

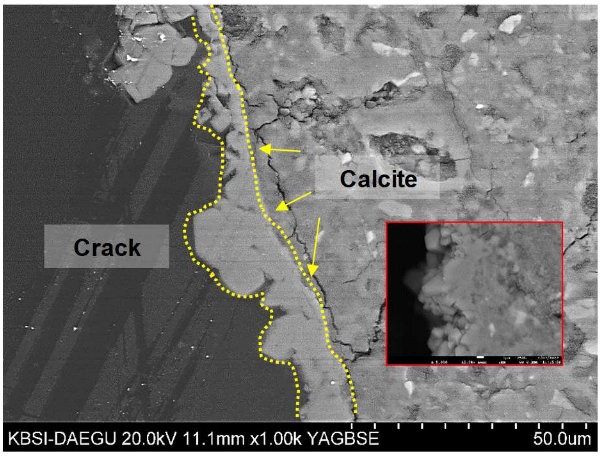

Fig. 7 SEM image in SH-M sample at HP 28 days.

4 Conclusion

This study evaluated the mechanical properties and self-healing performance of cement mortar using palmitic acid-coated PC, CSA, and Na$_2$SO$_4$ as SHMs. To this end, compressive strength tests, constant water head permeability tests, gas diffusion tests, optical microscope, and SEM measurements were performed. The experimental results are as follows.

- Palmitic acid coating of SHM increased the possibility of unreacted particles in the matrix by maintaining the water repellency of the powder for more than 24 hours.
- The incorporation of the SHMs improved the initial and 28-day compressive strength of the cement mortar by about 20%.
- As a result of the sealing efficiency evaluation for disc specimens with a crack width of 0.3 mm, incorporating inorganic SHM improved the sealing efficiency. However, there was a difference in the results according to the evaluation method. For this reason, a study on the compatibility between test methods is needed.
- From the crack internal observation results at HP 28 days, it was confirmed that $CaCO_3$ was precipitated as a major sealing product inside the cracks when the inorganic SHM was mixed. It was confirmed that precipitation of $CaCO_3$ contributed to improving cement mortar healing performance.

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