Study on Mechanism of Pore Modification by Polymer Particles

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Abstract. In recent years, deterioration of concrete structures has become a problem, and requires maintenance and repair. The cross-sectional repair method is frequently used to repair deteriorated structures. The material used in this method must have good adhesion to concrete and durability against the deterioration factors such as carbonation, chloride penetration and water permeability. In ordinary polymer cement mortars, the polymer particles bond together and make a polymer film, which improves the mass transfer resistance. Therefore, it is often used as a cross-sectional repair material. On the other hand, new developed core-shell polymer particles have dispersibility and two-layer structure of core and shell. In some cases, the addition of this polymer has been shown to have very high mass transfer resistance to water. However, the mechanism of the performance improvement has not been understood yet. The improvement in mass transfer resistance is thought to be due to the modification of the pore, which is a mass transfer pathway. In this study, we measured the porosity and conducted mass transfer resistance, and compared core-shell polymers with various materials which densifies the pores. For example, ordinary polymers that has films and silica fume which has a pore-filling effect with fine particles. In addition, by comparing several tests and expressing the state inside the pores, we investigated the mechanism of improving mass transfer resistance when core-shell polymer is added.

Keywords: Cross-sectional repair material; Polymer cement mortar; Core-shell polymer; Mass transfer resistance; pores structure

1. INTRODUCTION

In recent years, the number of reinforced concrete structures to be maintained has been increasing. Due to this, the demand for repair of structures has been increasing. There are many repair methods, and appropriate repairs should be carried out according to the cause of deterioration of the structure. When reinforcing bars are corroded, the cross-sectional repair method is often used. The deteriorated part is removed, and the reinforcing bars are treated with anti-corrosion product, and then the concrete is restored to its original state. Cross-sectional repair materials are required to have not only physical properties, such as strength, but also durability. In order to improve durability, it is important to prevent the penetration of degradation factors by reducing the pores, which are the pathways for the movement of materials. Since it meets the performance requirements, polymer cement mortars are often used as cross-sectional repair materials. In polymer cement mortar, polymer particles mixed into the mortar bond together to form a polymer film as the water that contains the polymer particles in the pores dries. Previous studies have shown that the presence of this film inside the pores improves the mass transfer resistance. However, since the film is formed by the flocculation of polymer particles, it may be unevenly distributed within the mortar. In this study, we attempted to use a newly developed core-shell polymer with high dispersibility, as shown in Figure 1. Core-shell polymers are composed of two layers: core and shell. The shell layer provides affinity with cement, and the performance can be divided into core and shell to show dispersibility. The mass transfer resistance and pore structure of mortar with core-shell polymer will be investigated by mass transfer test and porosity test.
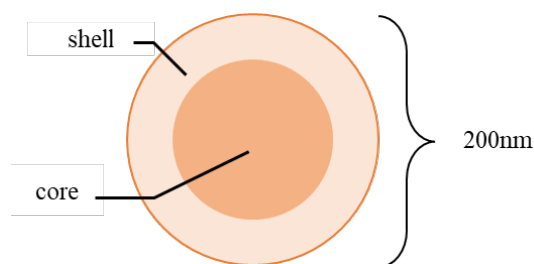

Figure 1. Core-shell polymers

2. OUTLINE OF EXPERIMENT

2.1. Materials and Mix Proportion of Mortar

Ordinary Portland cement was used as the cement, and core-shell polymers and conventional polymers were used. Core-shell polymers are polymers with a multilayered structure achieved by two-step emulsion polymerization. The core is made of acrylic rubber and the shell is made of acrylic polymer. Silica fume and C-S-H hardening accelerators were used as examples of comparatives methods to densify the pores, as one is an admixture of fine particles and the other is used for accelerating the hydration.

Table 1 shows the mix proportion of the mortar. The mix proportion was set at a constant water-cement ratio of 50% and cement: fine aggregate ratio was set at 1:2.3. The polymer was added at 5% of the cement by solids content, considering the solids concentration. In addition, a defoaming agent was used at 10% of the latex (Solution containing polymer) to prevent excessive air inclusion due to the surfactant contained in the latex. Silica fume was added in replacement of the cement, and C-S-H hardening accelerator and defoaming agent were added in replacement of the water. In this paper, the core-shell polymer is named CS, the conventional polymer is named NP, the silica fume is named SF, and the C-S-H hardening accelerator is ACX.

Table 1. Mix proportion of mortar

Sample Name		W/C (%)	S/C (%)	Addition rate (%)	Defoaming agent (%)
N	-			-	-
CS	Core-shell type	50	2.3	C×5	Latex×10
NP	Conventional type				
SF	Silica fume			C×5	-
ACX	C-S-H hardening accelerator			C×3	-

2.2. Testing Methods

After casting the mortar, the specimens were demolded at the age of 1 day and cured in water for 3, 7, 28 and 56 days. The following tests were carried out using the specimens with different curing days.

2.2.1 Water penetration test

Testing was performed in accordance with JSCE-G 582-2018. In the pre-treatment, the specimens of φ50 × 100 mm were dried after the curing periods. The specimens were placed in an environment of 40°C, 30% RH and dried until the weight became constant. The sides of the specimen were sealed with aluminium tape, and a depth of 1 cm from the bottom was immersed in water. The weight was measured after 5, 24 and 48 hours. After that, the specimens were split, sprayed with a moisture sensing agent, and the depth of coloration was measured. The amount of mass increase before and after immersion was defined as the penetration amount.

2.2.2 Air permeability test

The test was carried out using the output method with a disk-shaped specimen of φ100 × 20 mm. In the pre-treatment, the specimens that finished the curing period were dried. The specimens were placed in an environment of 40°C, 30% RH and dried until the weight became constant. Air was injected at 0.1 MPa, and after confirming that the air flow had become constant, the permeability was measured using a graduated cylinder by water displacement method. The permeability coefficient was calculated using the Darcy rule using the following equation (1)

$$K = \frac{2LP_1}{(P_1^2 - P_2^2)} \cdot \frac{Q}{A} \tag{1}$$

K: Air permeability coefficient (cm^4/N・s), L: Specimen thickness (cm), P$_1$: Loading pressure (N/mm^2), P$_2$: Outflow side pressure (N/cm^2), Q: Amount of air permeability (cm^3/s), A: permeable area (cm^2)

2.2.3 Porosity test

The specimen used in the water penetration test was crushed and a 25 mm square specimen was taken out. The samples were saturated with water by a vacuum desiccator. After measuring the saturated weight and the weight in water, the samples were left to dry at 40°C, RH 30% until their weights became constant, and the weight in an absolutely dry state was then measured. Porosity was calculated by Archimedes method. Three samples were tested and the average was used as the result.

3. RESULTS AND DISCUSSION

3.1. Mass Transfer Test

Figure 2 shows an example of results of the moisture penetration test after 7 days of curing. It shows the split surface of the test specimen after 48 hours of penetration. Figure 3 shows the amount of water penetration after 7 days of curing. The dark pink area indicates the area where the water has penetrated. The water penetration was smaller in CS and NP than in the other mixed materials. In other words, water penetration was suppressed by the addition of dispersed polymers as well as conventional polymers. Also, the depth of water penetration of SF is similar to that of N. Figures 2 and 3 show the results after 7 days of curing, and the hydration reaction by cement is not so advanced that there is no difference in water permeability due to the pozzolanic reaction, and the depth of water penetration is also similar.

Based on the trend of the slope, it is possible that different results could be obtained by conducting the test for more than 48 hours. However, it is considered that conducting the test over a longer period of time may result in incorrect evaluation of the moisture penetration results due to the influence of the test environment and other factors.

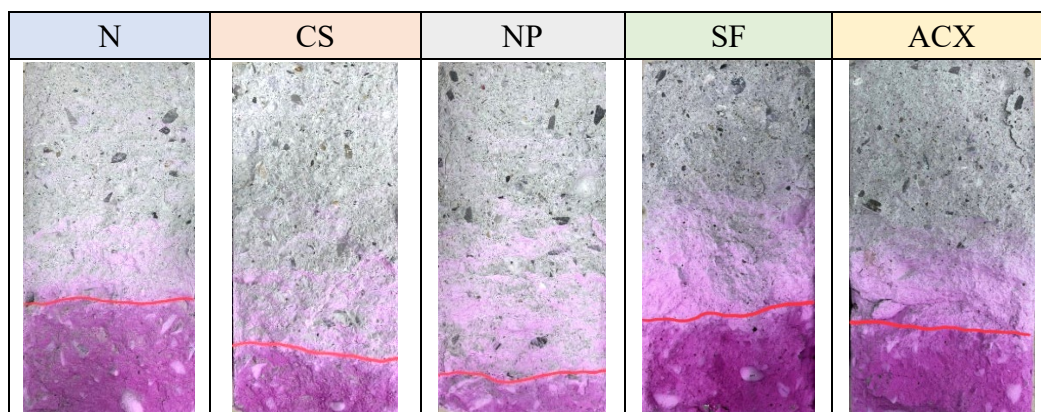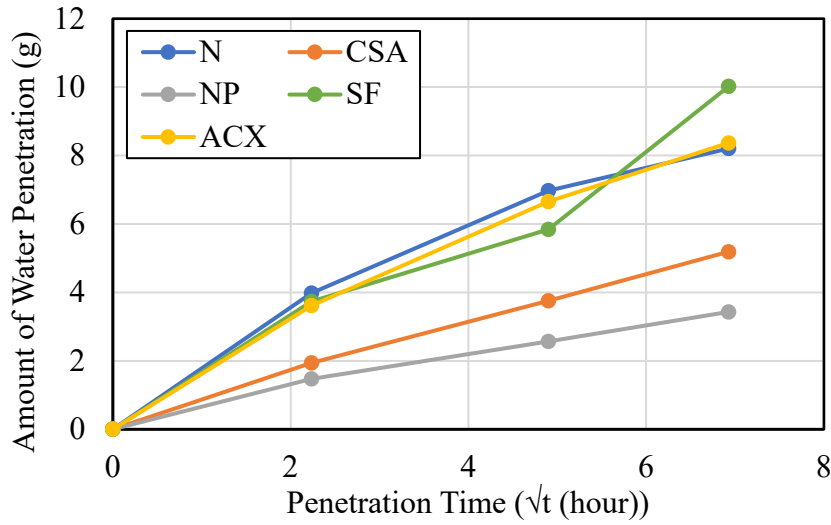| N	CS	NP	SF	ACX

Figure 2. Split surface of the test specimen after 48 hours of penetration

Figure 3. Results of water penetration test

The amount of water penetration was proportional to the square root of the penetration time, and the $\sqrt{t}$ law behavior was observed. This slope is shown in Figure 4 as the water penetration rate coefficient. The results of the air permeability coefficient calculated from the air permeability test are shown in Figure 5 It was confirmed that the water infiltration rate coefficient and air permeability coefficient decreased with the increase of curing days. It was also observed that the improvement in CS was inferior to that of NP in short-term curing, however in long-term curing, CS was same that of NP. In other words, the effect of CS polymer on mass transfer resistance was considered to have changed by the curing time. For SF and ACX, there is a large change in the decrease in air permeability, especially from short-term curing to long-term curing. Because of the pozzolanic reactivity of SF, the porosity became very small and the air permeability decreased significantly. Also, in ACX, the C-S-H nanoparticles contained in the C-S-H hardening accelerator acted as seeds for crystal growth during cement hydration, resulting in a significant decrease in air permeability.
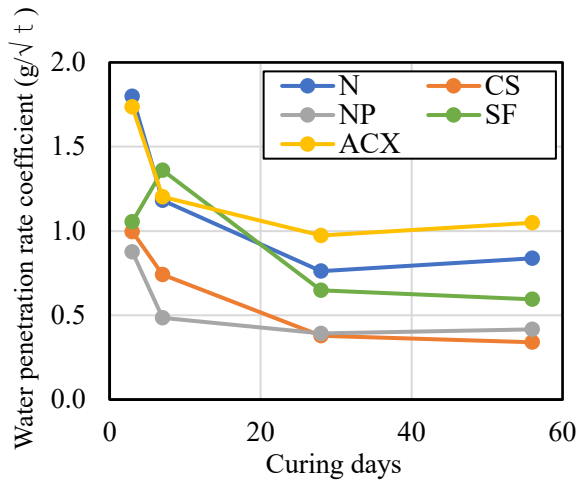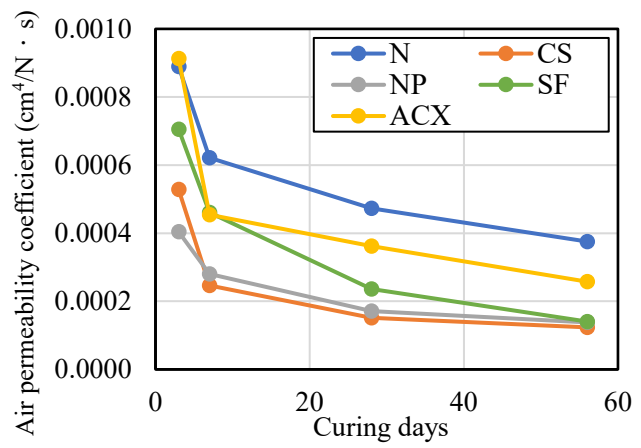
Figure 4. Water penetration rate coefficient

Figure 5. Air permeability coefficient

3.2. Relationship between porosity and air permeability coefficient

Figure 6 shows the relationship between porosity and air permeability coefficient. Regardless of the added materials, as the number of curing days increased, the air permeability decreased due to the decrease in porosity, but the trend was different between different materials added. SF and ACX show a decreasing trend similar to N, although the amount of change is different. The samples with polymer showed a different pattern. The permeability of NP decreased significantly from 3 days of curing compared to N and CS, and decreased gently with the passage of curing days. On the other hand, CS showed a decreasing trend similar to that of N when the curing days were short. Furthermore, the air permeability was different among the added materials even when the porosity was the same. These results suggest that there are differences in the characteristics of the pore structure.
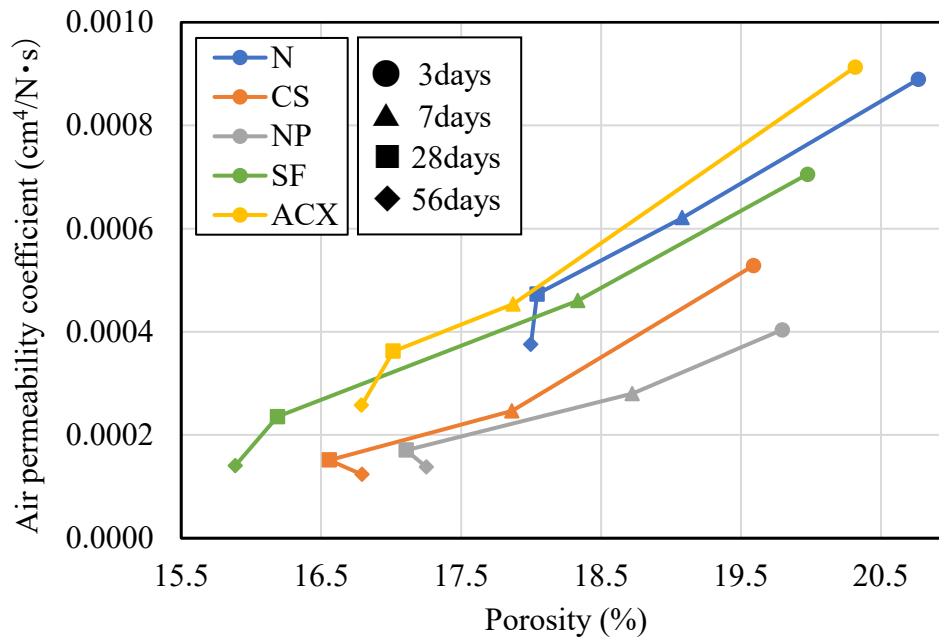
Figure 6. Relationship between porosity and air permeability coefficient

3.3. Consideration of pore structure

First, an image of the pore structure for each sample is illustrated in Figure 7. When ordinary Portland cement (N) is used, the hydration reaction of the cement progresses and the pore diameter decreases as the number of curing days increases. Therefore, the decreasing trend of N is due to the decrease in pore diameter. For SF and ACX, which showed the same trend as that of N, the trend is also considered to be due to the decrease in pore size. This may be because the pozzolanic reaction and the reaction by C-S-H nanoparticles are related to the hydration reaction. In the case of short curing, the air permeability of NP was greatly improved even though the hydration reaction of the cement was not sufficient and large pores were formed. This result suggests that NP exhibit very high mass transfer resistance after the drying process for film formation. On the other hand, CS tended to be close to N in short-term curing, suggesting that there was no film formation effect. In other words, the particles did not aggregate due to their high dispersibility and did not form a film. Therefore, CS is considered to have improved mass transfer resistance due to polymer particles. In the case of short curing, the apparent pore diameter decreased due to the filling of the pores by the particles, showing a similar trend to that of N. However, in the case of longer curing, the distance between the

polymer particles became closer, and the structure was more prone to inhibit mass transfer, which may have resulted in a mass transfer resistance comparable to that of NP.
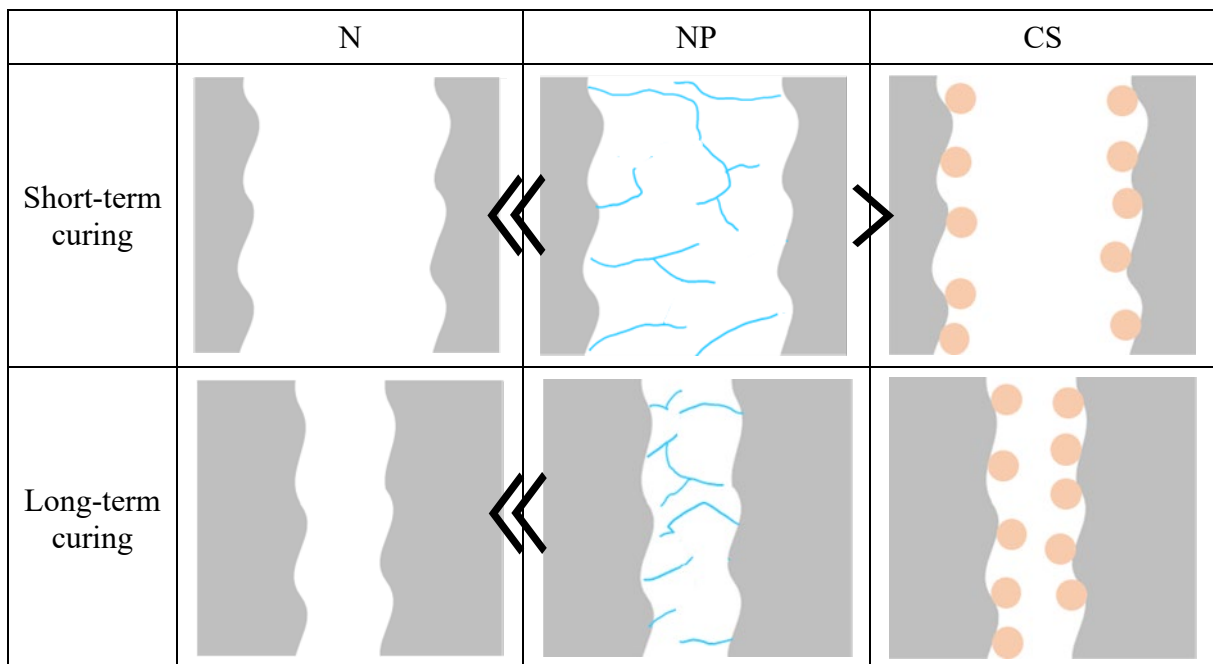
	N	NP	CS
Short-term curing			
Long-term curing			

Figure 7. Image of the pore structure

4 CONCLUSIONS

(1) The relationship between porosity and air permeability suggests that the mechanism of improving mass transfer resistance depends on the characteristics of the added material.

(2) It was inferred that while conventional polymers inhibit mass transfer by polymer film, core-shell polymers that are dispersive improve mass transfer resistance by having polymer particles dispersed and present in the pores.

(3) Even without the formation of a polymer film, the mass transfer resistance of CS is thought to be equal to or better than that of conventional products by promoting the hydration of cement.

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