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The control of response time in self-healing of granulated cementitious material by water-soluble film coating

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Abstract

Although various self-healing methods have been suggested until recently, these methods have merits and demerits. The utilization of cementitious material (e.g. expansive agent, mineral admixtures etc.) in various methods may be appropriate due to their good healing efficiency, compatibility with the cement matrix, and low cost, but the efficiency of healing products generated by necessity is not guaranteed. In this study, granulation/surface coating methods are applied to cementitious material. The self-healing time of materials can be controlled via water-soluble film thickness until cracks occur, and healing products will be formed because cementitious material react with moisture via the crack faces after water-soluble film was dissolved by moisture. It was verified through various tests that the granulated cementitious material with water-soluble film coating can control the time of self-healing and can prevent water migration via crack closing.

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Keywords: Self-healing; cementitious material; Granulation ; Surface coating; Water-soluble film

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1. Introduction

Because concrete has advantages such as simple manufacturing, economical, durability etc., it is being used widely as structural materials. However, it also has a number of disadvantages. The most typical disadvantage is crack. Various form's cracks may occur in most of concrete structures except prestressed concrete and it is impossible to prevent crack in concrete structures. Recently, construction techniques are focused to increment of service life and

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prevention of deterioration of existing structures via continual repair/maintenance. Also, durability design is applied to prevent deterioration factors in new structure. Crack that occurs in structures is required controlling measures because serviceability of structures is decreased. Repair method for infrastructures (e.g. nuclear power plants, offshore structures, tunnels etc.), which is difficult to repair, is demanded. Self-healing is a common phenomenon seen in a human body. Damage or injuries are automatically healed without any serious operation for themselves. Such a healing function is also provided in concrete. Actually, we have been aware of self-healing in conventional concrete. To our knowledge, the healing usually results from chemical reactions such as hydration and carbonation. Micro cracks are filled with a reaction product as long as reactants and water are available at the crack faces. However, it has not expected appreciable recovery in performances from the healing function. In Korea, self-healing of concrete has been conducted in very common studies such as self-healing properties of cement matrix, development of polymer composite and self-healing by using bacteria and so on. On the other hand, various self-healing strategies such as hollow fiber, microcapsule, expansive agent/mineral admixture, bacteria, and shape memory materials etc. have being conducted in Europe and Japan.

In this study, granulation/coating methods were applied to a cementitious material. The self-healing time of materials can be controlled via PVA film thickness until cracks occur, and healing products will be formed because the materials react with moisture via the crack faces after water-soluble film was dissolved by moisture. Application of granulation/coating method on cementitious material is combined of the advantage of microcapsule and expansive agent /mineral admixture. The appropriate water-soluble film thickness for the control of the self-healing time until crack occurrence was determined, and then all the specimens were immersed in water after the introduction of cracks. Afterwards, the crack widths and images were obtained via microscopy investigation depending on the elapsed time. At the same time, a water passing test was conducted, and the dynamic modulus of elasticity was measured.

2. Experimental procedure

2.1. Materials and mix proportion

Expansive agent that used commonly is to include lime or CSA. The CSA-based expansive agent consists of hauyne ($3CaO\cdot 3Al_2O_3\cdot CaSO_4$), free lime ($CaO$), and anhydrite ($CaSO_4$). The CSA-base expansive agent causes the expansion, which occurs by ettringite, calcium hydroxide, which were formed due to hydration reaction. Expansion mechanism is mainly achieved by formation of ettringite, but a factor is important because ettringite is influenced by time and manner of formation and shape. Therefore, although crack-closing is able to achieve by healing products which, formed ettringite and calcium carbonate when CSA-based expansive agent is only used, a limitation of dense degree may be existed. Therefore, Cement that forms stable C-S-H and sodium carbonate (Na_2CO_3) were added with CSA-based expansive agent in this study, and then they were granulated. Insoluble calcium carbonate ($CaCO_3$) is formed by reaction between sodium carbonate (Na_2CO_3) and calcium hydroxide ($Ca(OH)_2$), which is formed by C_3S, β-C_2S hydration and from CSA-expansive agent. Calcium carbonate is known as main products for filling crack faces. Table 1 indicates properties of sodium carbonate.

Table 1 Properties of sodium carbonate.

	Density (g/ml)	Molecular (g/mol)	Boiling point (°C)	Melting point (°C)	Solubility
Na_2CO_3	2.532	105.99	1600	851	29.4g/100g Water (25°C)

In this study, a cementitious material was granulated through a process involving kneading, wet granulation, and drying. And then the surface of the granule was coated with a water-soluble polymer substance using polyvinyl alcohol (PVA) for controlling self-healing time. By repeating coating process, the coating thickness was increased. The PVA coating was 0.012-0.0073 mm thick when the process was repeated at least twice. Mortar mixtures to evaluate self-healing efficiency were designed based on W/C=0.4 and with a cement-to-sand ratio of 1:3, according to ISO 679. Cement that used in this study is the Portland cement of Type Ⅰ (OPC) and aggregates used fine aggregate that collected in the Ongjin. Table 2 summarizes properties of cement and fine aggregate, which are mainly used in this study.

Table 2 properties of cement and fine aggregate.

Component	Properties
Cement	● Physical : Specific gravity - 3.14 g/cm2, Sruface area - 3460 cm2/g, Ignition loss - 1.2% ● Chemical : SiO_2 (20.6%), Al_2O_3 (6.1%), Fe_2O_3 (3.4%), CaO (62.1%), MgO (2.9%), SO_3 (2.1%)
Fine aggregate	● G_{max} : 5mm, Density : 2.60 g/cm^3, Absorption : 1.05%, F.M. : 2.78, Chloride contents : 0.01%, Unit weight : 1.565 kg/L

Also, the replacement ratio of the granules with PVA coating was limited to 10% by mass cement because some researchers noted the occurrence of unexpected expansion. At the age of 28 days, cracks (range: 0.1-0.35 mm) were created in the mortar specimens by means of a three-point bending test. Then the crack widths and images were obtained via microscopy investigation. Also, self-healing efficiency was evaluated by a water passing test and measurement of dynamic modulus of elasticity. Table 3 indicates Mortar mix proportion for evaluation of self-healing efficiency.

Table 3 Mortar mix proportion for evaluation of self-healing efficiency

W/C (%)	Unit Weight (g/batch)			Remark
	Water	Cement	Fine aggregate	
40.0	180	450	1350	1:3

2.2. Experimental method

To verify healing efficiency of mortar specimens incorporating Granule with PVA film coating, which was determined via length change test, cracks should be introduced prior to test for verifying healing efficiency. In general, cracks targeted by healing are induced by mechanical loading of flexure or tension. Freezing-thawing cycles are also sometimes used because of convenience of inducing micro cracks. In this study, all the mortar mixtures were placed into the 40X40X160mm moulds in different layers. First, a 10mm mortar layer was brought into moulds and was compacted via vibration. Two Φ2mm reinforcement bars were placed onto this layer. Afterwards, the moulds were further filled with mortar. After casting, mortar prisms were cured at 20±2℃ and in a 95±5% humidity chamber until the testing time. At the age of 28 days, cracks (range: 0.01-0.35 mm) were created in the mortar prisms by means of a three-point bending test. All the specimens were immersed in water after the introduction of cracks. Afterwards, the crack widths and images were obtained via microscopy investigation depending on the elapsed time. Although recovery of crack on surface of specimen can be monitored via microscope, crack inside specimen is unable to monitor via microscope. Therefore, a dynamic modulus of elasticity was measured at the same time, when microscopy investigation was conducted, according to ASTM C 215. Basically, a test specimen (either a cylinder or a prism) is supported at its nodal point so that it may undergo free-free vibration without significant restriction (i.e., for transverse vibration, it is supported at 0.224 of the length from each end of the specimen; for longitudinal or torsional vibration, it is supported at the center). Subsequently, achievement of internal crack-closing was evaluated based on the relative dynamic modulus of elasticity by using Equation 1. The relative dynamic modulus of elasticity was determined based on the percentage of dynamic modulus of elasticity before and after the crack introduction depending on the elapsed time.

$$P_t = \left(\frac{E_t^2}{E_0^2}\right) \times 100 \qquad (1)$$

Where, P_t is the relative dynamic modulus of elasticity depending on elapsed time, E_0 is a dynamic modulus of elasticity before introduction of crack, E_t is a dynamic modulus of elasticity depending on elapsed time after introduction of crack.

Finally, a water passing test for, which evaluated prevention of aggressive agents such as the migration of water due to crack propagation, was conducted for 300min about specimens of same size (40X40X160mm), when microscopy investigation was conducted. Healing efficacy was evaluated via water permeability coefficient that was calculated by using Equation 2.

$$k = \frac{aL}{At} ln(\frac{h_1}{h_2}) \qquad (2)$$

Where k is water permeability coefficient (mm/s), a is the cross-sectional area of the pipette (mm^2), L is the specimen thickness (mm) , A is the cross-sectional area of the specimen (mm^2), t is the time (seconds), h_1,h_2 are the initial and final water heads(mm).

3. Results and discussion

3.1. Evaluation of healing efficiency via crack-width in change

After introduction of cracks (range: 0.01-0.35 mm), they were immersed in water, and the crack widths and images were obtained via microscopy investigation depending on elapsed time. Fig. 1 indicates the changes in the crack width of each mixture (Plain, Granule-Cm) depending on the elapsed time.

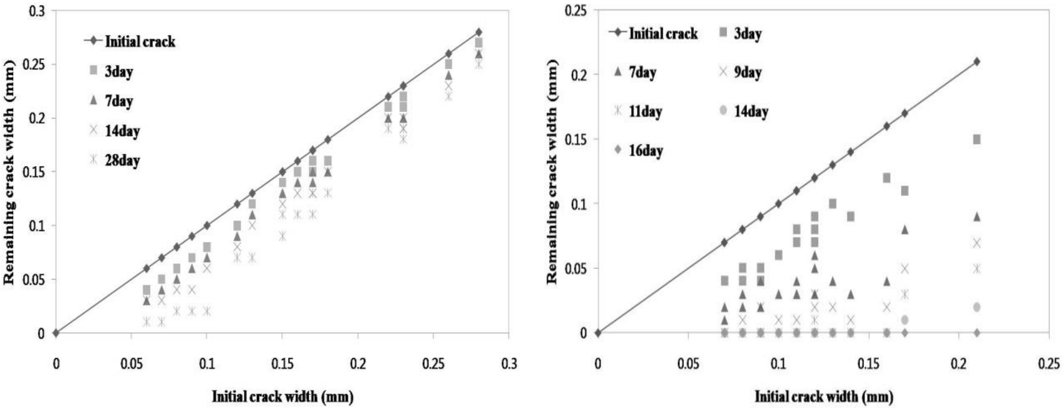

Fig. 1 Changes in the crack width at each observation day; (Left) Plain (Right) Granule-Cm

In Fig. 1, Plain shows that crack-closing was not achieved completely in all the crack widths up to 28 days elapsed time. Although the <0.1 mm crack width was not completely closed, as reported in the previous researches such as Jaroenratanapirom et al., it showed a similar crack-closing. For granulated cementitious material with PVA film coating (Granule-EA), the <0.1 mm, 0.1-0.2 mm, and >0.2 mm crack widths indicate complete crack-closing within 11, 14, and 16 days, respectively. Therefore, it was verified that cementitious material of the inside might have reacted with water because the water-soluble PVA film was dissolved by the migrated moisture via the crack faces. As a result, crack-closing was achieved.

3.2. Evaluation of healing efficiency via dynamic modulus of elasticity

Although recovery of crack on surface of specimen can be monitored via microscope, crack inside specimen is unable to monitor via microscope. Therefore, a dynamic modulus of elasticity was measured at same time, when microscopy investigation was conducted. Subsequently, relative dynamic modulus of elasticity was calculated by using equation 1. The internal crack-closing was evaluated based on the relative dynamic modulus of elasticity, which was determined based on the percentage of dynamic modulus of elasticity before and after the crack introduction depending on the elapsed time. Fig. 2 indicates relative dynamic modulus of elasticity for Granule-Cm compared with Plain.

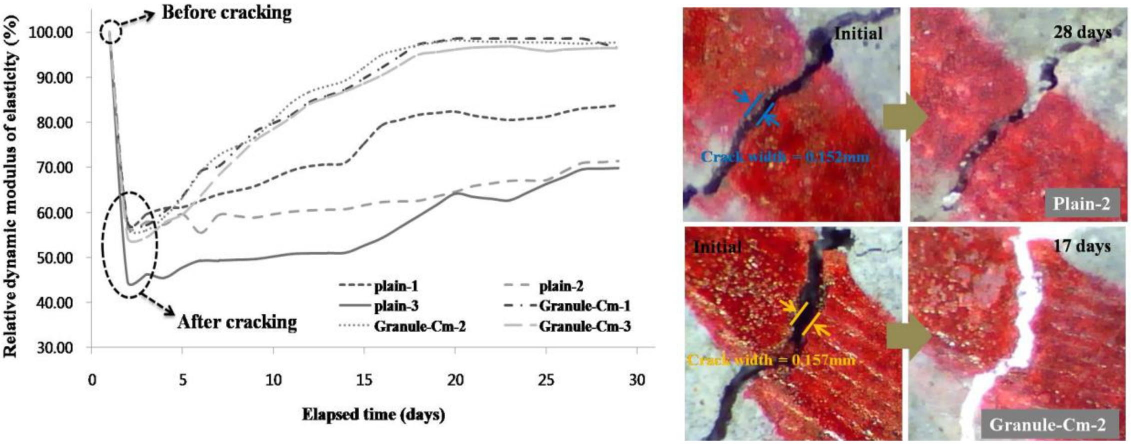

Fig. 2 Granule-Cm Comparison of relative dynamic modulus of elasticity and crack images (1 : <0.1mm, 2 : 0.1mm~0.2mm, 3 : >0.2mm)

In Fig. 2, the mean relative dynamic modulus of elasticity in all the specimens showed a sharp decrease when cracks were created. The mean relative dynamic modulus of elasticity of Plain-1 reached about 80% of the state before the introduction of cracks, with a gradual increase depending on the elapsed time, and those of Plain-2 and 3 reached about 60%. Therefore, this indicates that Plain was not achieved complete internal crack-closing. Also, relative dynamic modulus of elasticity of all mixtures, except for Plain, is over 90% at 28-days age. In particular, most of specimens had recovered relative dynamic modulus of elasticity after 14-days. This can be supposed that the specimens, which incorporated Granule with PVA film coating, were achieved internal crack-closing because cementitious material of the inside might have reacted by the migrated moisture via the crack faces.

3.3. Prevention of water migration by crack-closing

Most of crack do not affect the ability of concrete to carry load, but may affect the durability of the concrete by providing points of easy access to the inside of the concrete for aggressive agents. Therefore, Self-healing improvement plays an important role in the prevention of water migration rather than in the recovery of the mechanical properties. Therefore, a water passing test, which evaluated prevention of aggressive agents such as the migration of water due to crack propagation, was conducted at same time when microscopy investigation was conducted. Fig. 3 indicates comparison of water permeability coefficient on each crack width range for Granule-Cm.

In Fig. 3, it indicates that a similar water permeability coefficient shows for each crack width range of (<0.1 mm, 0.1-0.2 mm, >0.2 mm). In particular, unlike the crack closing results mentioned above, the water permeability coefficients of Plain-2 and 3 did not significantly differ in state after the introduction of cracks, and that of Plain-1 slightly decreased. Granule-Cm indicates low water permeability coefficient compared to Plain-1 at 28-days. Also, although water permeability coefficient of Plain was decreased depending on crack width range, that of Granule-Cm is similar regardless of crack width range. Therefore, the efficacy of crack closing, which prevents water migration through the self-healing of Granule with PVA film coating, was verified.

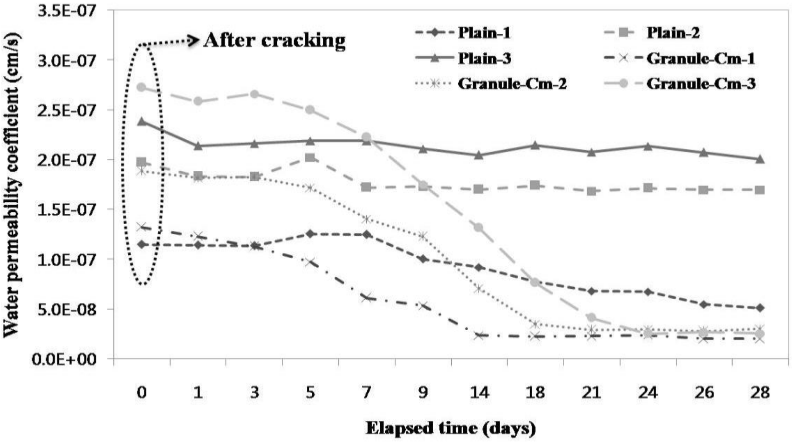

Fig. 3 Water permeability coefficient on each crack width range (1 : <0.1mm, 2 : 0.1mm~0.2mm, 3 : >0.2mm)

4. Conclusion

In this study, the appropriate PVA film thickness for the control of the self-healing efficacy until crack occurrence was determined and then healing efficiency was evaluated by testing. As a result, it was verified that the granulated cementitious material with PVA film coating can control the self-healing efficacy of healing materials by PVA film until cracks occur and can prevent water migration via crack closing.

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