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Development of anti-fungal mortar and concrete using Zeolite and Zeocarbon microcapsules

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ABSTRACT

Anti-fungal mortar and concrete are developed using micro-encapsulated fungus-resisting material. D-Limonene is selected for the core anti-fungal material and Zeolite and Zeocarbon are used for reinforcing the capsule membranes. Damage and survival possibilities of microcapsules in the casting stage of mortar and concrete are examined by scanning electron microscopy (SEM) and high pressure liquid chromatography (HPLC). Several tests are conducted to evaluate the effects of microcapsule additions on the properties of fresh and hardened mortar and concrete. Anti-fungal effectiveness of the developed mortar is verified by mock-up panel tests, in which resistance to fungus growth on the panel surface is studied.

1. Introduction

The high alkalinity of mortar and concrete is known to prevent bacteria and fungus from growing on their surface. However, as neutralization (or carbonation) progresses, microorganisms such as bacteria and fungi begin to colonize on or within concrete. When the structures are exposed to moist conditions for a prolonged period of time, the population of microorganisms can spread out easily. Concrete containing such organisms usually suffers from one or more of the following problems: (a) corrosive chemicals released by their metabolism; (b) creation of an environment that promotes corrosion of steel; (c) creation of open porosity due to penetration by insects and (d) formation of unsightly stains on the surface of concrete [1]. When organisms are growing inside a building, discomforting odor can occur and structure inhabitants can be infected with harmful diseases [2,3].

Regarding prevention of fungi growth and spread in mortar and concrete, the direct addition of fungicidal admixtures in the casting stage of mortar and concrete is known to be effective [4–6]. However, the fungicidal effect of direct addition can be transient and there are needs for longer-lasting alternatives. Another possible preventive method is to coat fungicidal substances on mortar and concrete surfaces. This method has limitation of only being applicable to the surface subjected to light abrasion [1,7,8]. Other possible remedy is to eliminate fungus friendly environmental conditions for their growth. The best way to setup environmental conditions to prevent fungus growths is to minimize moisture level, eliminate dew formed surfaces, perform dehumidification, and control temperature. However, these methods are rather time-consuming and expensive for common usage. Also, these methods do not completely eliminate fungus problems inside of mortar and concrete. For the chemical compositions of fungicidal admixtures, the generic toxicant substances such as polyhalogenated phenols, copper acetoarsenite, and copper arsenite are used [1]. These substances are effective in preventing fungi from spreading, but also can be harmful to the inhabitants of structures [7]. Since the previously implemented anti-fungal methods have limitations and chemical toxicity, safer, effective, and less toxic anti-fungal methods have to be developed.

In this study, in order to effectively eliminate fungi from growing in concrete structures, a novel method of adding anti-fungal microcapsules into mortar and concrete during their casting stage is developed. Micro-encapsulation of a natural biocidal substance is used as a solution for the prolonged toxicity problem. Microcapsules release the fungicidal core substance and the release rate can be controlled by varying the thickness of their permeable membranes. The physical performance and anti-fungal effect of mortar and concrete containing microcapsules are verified through experimental works.

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2. Development of anti-fungal microcapsules

2.1. Anti-fungal microcapsule development

The anti-fungal core material of microcapsules is selected as D-Limonene. D-Limonene is natural biocidal substance from orange. An emulsion is created by mixing surface active agent and core material using a homo-mixer to control the thickness and particle size. Then, the microcapsules are produced by adding melamine and formaldehyde prepolymer solvents and agitating the mixture at 55–65 °C. Since the membrane of microcapsules is created using melamine and formaldehyde, polymer may pre-maturely rupture in the mixing and casting stages of mortar or concrete. In this study, for preventing premature rupture, Zeolite or Zeocarbon is used for the membrane reinforcement. Zeolite and Zeocarbon have an ability to withstand high friction or impact, which may occur during the mixing and casting process of mortar or concrete. The basic concept of anti-fungal microcapsule is shown in Fig. 1 and the manufacturing process is described in Fig. 2 [9–12].

From long term observations of the behavior of the anti-fungal mortar, anti-fungal core material is gradually and slowly released out. Based on the preliminary tests, releasing time to empty the microcapsule is calculated from 5 to 10 years [2]. However, by controlling the thickness and other parameters of microcapsules, the duration of the anti-fungal effect can be controlled.

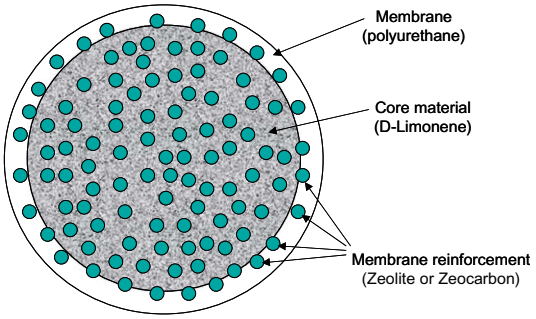


Fig. 1. Composition of anti-fungal microcapsule.

2.2. Manufacturing

For manufacturing Zeolite reinforced microcapsules, Zeolite powder and D-Limonene are mixed in the first stage. Then, polyurethane is added to the mixture. After mixing process, capsules are formed by granulating and coating. Fig. 3 shows the photo of shape and size of Zeolite reinforced microcapsules taken using an optical microscope. In case of Zeocarbon added microcapsules, Zeocarbon and D-Limonene are mixed firstly. Then, capsules are formed by adding surface-active-agent of melamine and formaldehyde prepolymer solvent. Fig. 4 shows the photo of shape and size of Zeocarbon added microcapsules taken using an optical microscope. Agitating time and surrounding temperature are 150 min and 55–65 °C, respectively.

2.3. Verification

2.3.1. Antibiotic test

Antibiotic tests of the developed microcapsules were carried out by *Korea Institute of Construction Materials* (*KICM*). The test results are tabulated in Table 1. The bacilli used in the tests are *Escherichia coli ATCC 25922* and *Staphylococcus aureus ATCC 6538*. The test data shows that the decrements of bacilli for colon and pyogenic are 99.8% and 99.7%, respectively. The results show that the developed microcapsules have excellent antibiotic performance.

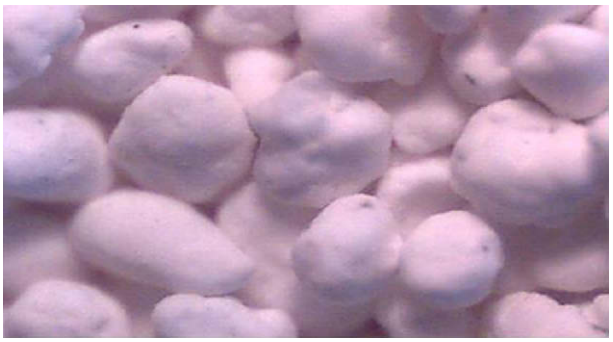


Fig. 3. Zeolite type microcapsules viewed by optical microscope (500–1000 μm).

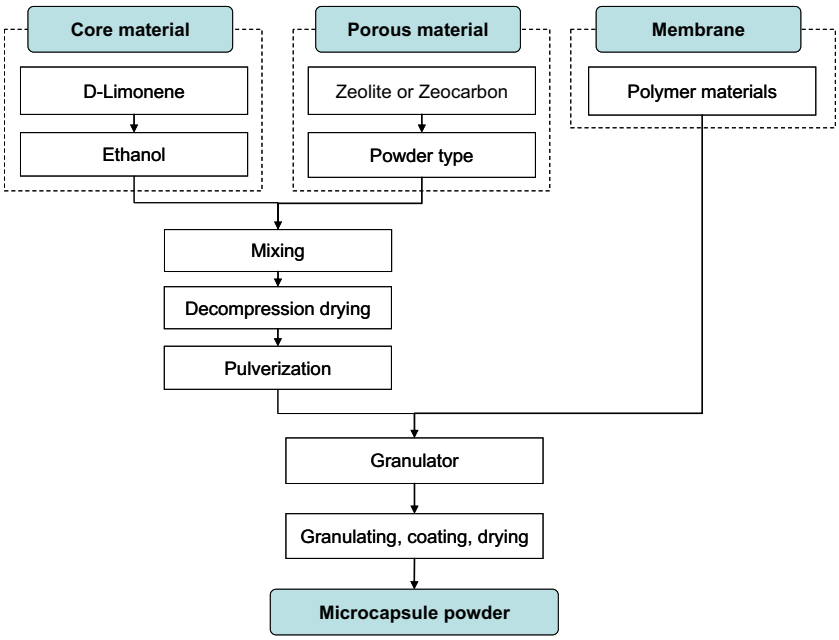


Fig. 2. Manufacturing process of microcapsule.

Fig. 4. Zeocarbon type microcapsules viewed by optical microscope (290–680 μm).

2.3.2. Toxicity test

Toxicity tests of the developed capsules were performed at *Korea Apparel Testing and Research Institute* (*KATRI*). The test results are tabulated in Table 2. The tests were performed with the test method of acute oral toxicity by using ICR mouse [13]. In acute oral toxicity test, one dose of 2000 mg/kg capsule material is orally injected into 5 week old male and female mice. Then, mortality rate, clinical sign, and weight change are checked 2 weeks later. Table 2 shows that all of LD50 are greater than 2000 mg/kg, where LD50 means injected amount for 50% of Lethal Dosage. Therefore, the developed microcapsule material satisfies the safety requirement of a minimum amount of 2000 mg/kg [14].

3. Performance evaluation of mortar and concrete containing microcapsules

When microcapsules are added to mortar and concrete, the problems of clustering and damage of membrane can occur during mixing and casting. So, microcapsule should ensure dispersibility and surface hardness. Addition of microcapsules can also affect the physical properties of fresh and hardened mortar and concrete such as workability and strength. In this study, the physical properties and performances of mortar and concrete containing antifungal microcapsules are evaluated by appropriate tests.

3.1. Mortar containing microcapsules

3.1.1. Microcapsule sustainability

For the assessment of applicability of developed microcapsules, the test specimens of paste and mortar specimens are prepared as shown in Table 3. For grouping of microcapsule sizes, 4 and 1 groups are selected for Zeolite and Zeocarbon groups based on their average diameter ranges, respectively. A comparative control specimen without microcapsule is designated as plain. For all test specimens, 5% of microcapsules are added by weight fraction of cement amount. Damage level and sustainability of microcapsule were assessed by scanning electron microscope (SEM). Morphology of

Table 1
Results of antibiotic test for microcapsule.

Tested bacillus type	Sample type	Number of bacillus[d]		Decrement of bacillus (%)
		Initial density (CFU[b]/40P[c])	Density after 24 h (CFU/40P)	
Colon bacillus	Blank[a]	426	1189	–
	Antibiotic microcapsule	426	1	99.8
Pyogenic bacillus	Blank	312	714	–
	Antibiotic microcapsule	312	1	99.7

[a] Blank: microcapsules are not included.
[b] CFU: Colony forming unit.
[c] 40p: 0.04 mL.
[d] Number of bacillus is calculated by multiple dilution.

Table 2
Mortality and clinical sign to treatment.

Sex	Dose	No. of animal tested	Clinical signs	Final mortality
Male	>2000 mg/kg	5	NAD[a]	0/5[b]
	0	5	NAD	0/5
Female	>2000 mg/kg	5	NAD	0/5
	0	5	NAD	0/5

[a] NAD: no abnormalities detected.
[b] Values are expressed as number of dead animals/number of total animals tested.

Table 3
Experimental conditions and symbols of specimens.

Type of microcapsule (5% of cement content)		Paste (W/C = 40%)	Mortar (W/C = 60%)	Mortar + SP[a] (W/C = 60%)
Plain		PP	MP	MAP
Zeolite added	2 mm over MC[b]	P-1	M-1	MA-1
	1–2 mm MC	P-2	M-2	MA-2
	500–1000 μm MC	P-3	M-3	MA-3
	150–500 μm MC	P-4	M-4	MA-4
Zeocarbon added	290–680 μm MC	P-5	M-5	MA-5

[a] SP: superplasticizer.
[b] MC: microcapsules.

mortar containing microcapsules captured by SEM is shown in Fig. 5. For all specimens, microcapsules are clearly observed to be undamaged. The comparison of SEM photos shows that microcapsules in the specimens are undamaged after the process of mixing and casting.

3.1.2. High pressure liquid chromatography analysis

High pressure liquid chromatography (HPLC) analysis was carried out for quantifying damage state of microcapsule in the specimens. The destruction rate of the capsules is examined by measuring the quantity of the core material dissolved in the solvent (Hexane). For this test, the microcapsules are prepared in several clusters of different size for clear observations. The measured values are compared with the theoretical assumed values of 100% destructed capsules as shown in Table 4. When Zeocarbon type microcapsule is used, the destruction rate of capsule is 6.6%, which is the highest stability according to the HPLC analyses.

3.1.3. Physical properties

Compressive strength and shrinkage tests were performed on mortar containing anti-fungal microcapsules. Zeocarbon microcapsules were used for the anti-fungal mortar based on the results of previous sustainability tests. General decorative mortar (weight ratio of sand to cement is of 3 to 1) was used and the microcapsules were added according to the two different adding ratios as shown in Table 5.

Compressive strength tests were carried out on the 28 days aged specimens and the results are shown in Table 6. When 5% and 15% of microcapsules are added to mortar, compressive strength of mortar decreases by 6% and 10.5%, respectively. The more microcapsules are added, the less compressive strength is produced.

Shrinkage test results of the mortar containing microcapsules are shown in Fig. 6. The beginning portion before 14 days and the last portion after 60 days of the graph show unusual behavior compared to common shrinkage behavior. This might due to different test conditions and measuring errors. However, the global shrinkage trends are consistent from the beginning to the end, so the relative comparison of each strain value at each point should be evaluated. The maximum drying shrinkages of mortar are 1.890×10^{-4} and

Table 5
Mix proportion of mortar.

MC addition ratio	Mixed contents (g)			
	Water	Cement	Sand	MC
0%	294	490	1470	0
5%				24.5
15%				73.5

Table 6
Compressive strength test results of mortar containing microcapsules

Microcapsules addition ratio	Compressive strength	Strength reduction rate
0%	13.4 N/mm^2	Reference
5%	12.6 N/mm^2	6.0%
15%	12.0 N/mm^2	10.5%

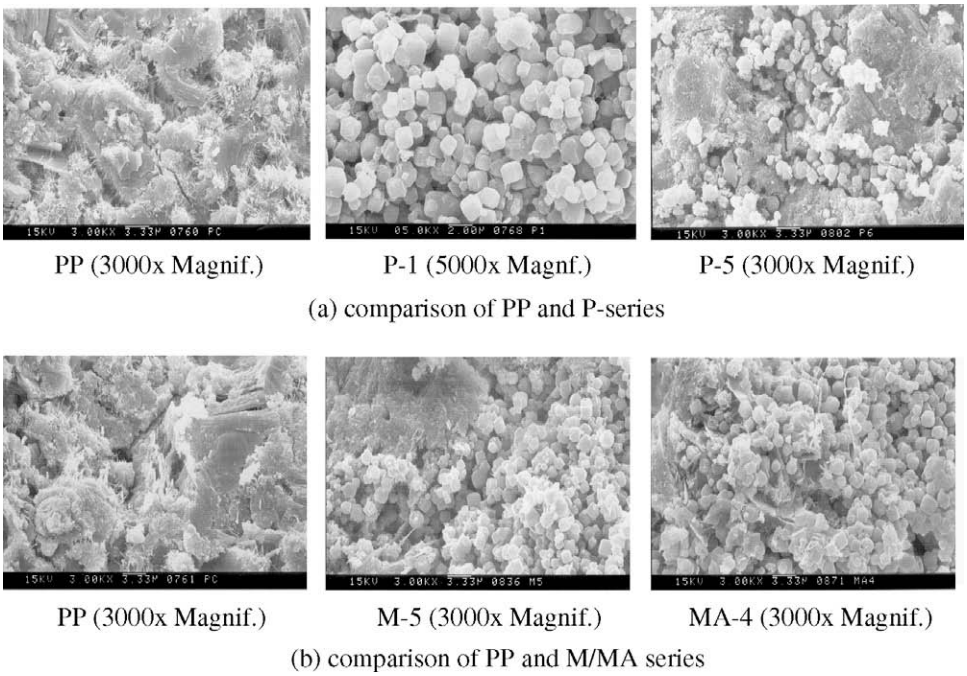


Fig. 5. Morphology of mortar containing microcapsules.

Table 4
HPLC test results.

MC	Zeolite type			Zeocarbon type
	1000–2000 μm	500–1000 μm	150–500 μm	290–680 μm
Theoretical value (100% destruction)	30.3 μm/ml	30.3 μm/ml	30.3 μm/ml	32.4 μm/ml
Value measurement	2.57 μm/ml	2.53 μm/ml	2.40 μm/ml	2.13 μm/ml
Damage proportion	8.5%	8.3%	7.9%	6.6%

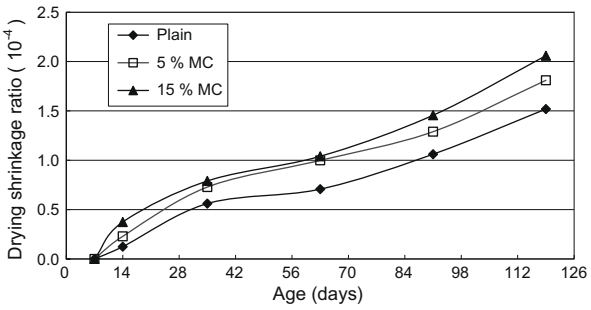


Fig. 6. Drying shrinkage of mortar.

2.059×10^{-4} with adding ratios of microcapsules of 5% and 15%, respectively. These are 24% and 35% higher drying shrinkage than the drying shrinkage of the plain mortar of 1.518×10^{-4}.

In conclusion, as more microcapsules are added into the mortar, compressive strength of mortar decreases and drying shrinkage of mortar increases. The reason for the lower compressive strength and higher drying shrinkage for the larger addition amount of microcapsules is due to the fact that the failure strength of the microcapsule is significantly lower than the failure strength of plain mortar and microcapsules can be considered as micro pores during the hydration process of mortar.

3.2. Concrete containing microcapsules

Slump, air volume, compressive strength, and bond strength tests were performed on concrete containing microcapsules. The microcapsules of Zeolite groups and Zeocarbon were added into concrete by 6.8% of cement weight. Mixture design of microcapsule added concrete specimen is shown in Table 7. The designed compressive strength of concrete is 20.6 MPa.

3.2.1. Workability

The slump test was conducted to evaluate the workability of concrete containing microcapsules and the results are shown in Table 8. Concrete with Zeolite group microcapsules has the slump range of 5.6–8.6 cm, which is an increase of 24.4–91.1% compared to the plain concrete. For the concrete with Zeocarbon microcapsules, the slump is 7 cm, which is an increase of 57.4% compared to the plain concrete. The results show that slump variation of concrete containing microcapsules depends on the size of microcapsules and the smaller size of microcapsules contributes to better workability of concrete. Adding microcapsules increase concrete workability, since microcapsules in concrete can cause ball bearing effect during the mixing stage.

(a) mortar panel specimen containing microcapsules

(b) specimen set with wooden formworks

Fig. 7. Preparation of mortar panel specimens containing microcapsules.

3.2.2. Air-volume

Air volume test was conducted and the results are presented in Table 8. The results show that the concrete with Zeolite group microcapsules has air-volume ratio of 4.4–5.6%, which is an increase of 29.4–64.7% compared to the plain concrete. For the concrete with Zeocarbon microcapsules, air-volume ratio is 4.1% which is an increase of 20% compared to the plain concrete.

Table 7
Mix proportion of concrete.

Standard design comp. strength (N/mm^2)	W/C (%)	s/a (%)	Unit weight(kg/m^3)				
			Cement	Water	Fine aggregate	Coarse aggregate	Microcapsules
20.6	51	35	349	178	642	1203	23.7

Table 8
Measured properties of concrete containing microcapsules.

Type and size of microcapsule		Slump (cm)	Slump increase (%)	Air content (%)	Air content increase (%)	Compressive strength, 28 days (MPa)	Compressive strength decrease (%)
Plain concrete		4.5	–	3.4	–	33	–
Zeolite type	2 mm over	5.6	24.4	4.4	29.4	31	6.1
	1–2 mm	6.5	44.4	4.6	35.3	30.5	7.6
	500–1000 μm	8.6	91.1	5.6	64.7	29	12.1
	150–500 μm	8.4	86.7	5.1	50.0	28.7	13
Zeocarbon type	290–680 μm	7.04	57.4	4.08	20	29.44	10.8

3.2.3. Compressive strength

Compressive strength test was carried out on the specimens cured for 28 days and the results are shown in Table 8. The compressive strengths of concrete with the Zeolite group microcapsules have the range of 28.7–31.0 MPa. The compressive strength of concrete containing microcapsules decreases by 6.1–13.0% compared to the plain concrete. For the concrete with Zeocarbon microcapsules, compressive strength is 29.4 MPa, which is a decrease of 10.8% compared to the plain concrete. Microcapsules seem to have larger effect on the strength reduction of concrete than that of mortar, even though it depends on the size of microcapsules.

4. Anti-fungal effectiveness of mortar containing microcapsules

Mock-up tests were conducted to verify the anti-fungal effect of microcapsule mortar on the surfaces of an actual structure. Three different types of mortar specimen were prepared with 0%, 5%, and 15% additions of Zeocarobon-type microcapsules. The mortar panel specimens are shown in Fig. 7. Wooden mold was used for better fungus growing conditions.

Micro-organisms extracted from milk are used to create fungus. Since fungus does not grow within a short period of time after placing of mortar due to its high alkalinity, the test specimens are exposed to outdoor condition for 60 days. After 60 days of outdoor exposure, the specimens are relocated to indoor condition with high humidity and poor ventilation, then the prepared micro-organisms are applied on the surface of panel specimens using brush. After 30 days of application of micro-organism, the surfaces of specimens are observed. Fungi are observed on the surface of the plain mortar specimen as shown in Fig. 8. Unfortunately, the color of fungi developed on the surface of plain mortar specimen is similar to the color of stains on the surface from the curing and exposure process. In order to clarify the fungus developed area, magnified photos are taken as shown in Fig. 8. In the magnified photos, anti-fungal effect of the mortar specimens containing microcapsules is evident.

After 45 days from first observation of fungus, the surface of the plain mortar specimen is covered with fungi as shown in Fig. 8. On the contrary, no fungus is observed on the surfaces of mortar specimens with 5% and 15% additions of microcapsules. Since the mortars with 5% and 15% microcapsule additions showed similar fungal-resistance characteristics, 5% addition of the anti-fungal microcapsules into mortar appears to be sufficient for preventing fungus from growing and spreading, at least for the time periods considered within this study.

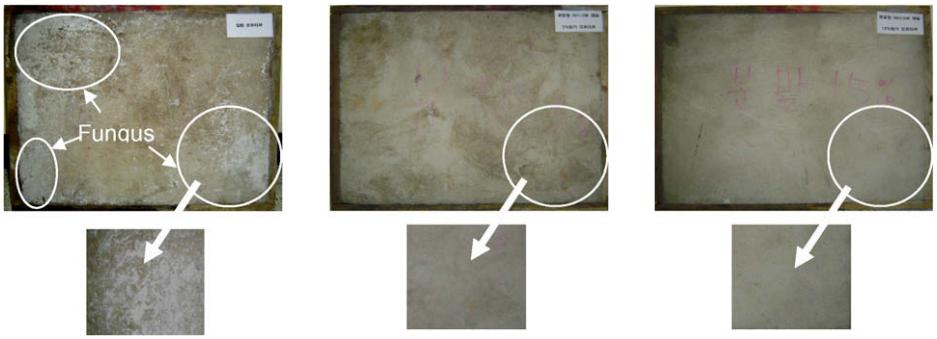
5. Conclusions

Anti-fungal mortar and concrete were developed by using micro-encapsulated biocidal materials. Experimental tests were conducted to verify the applicability and fungal-resistance of mortar and concrete containing these microcapsules. The conclusions of this study are as follows:

1. Zeolite and Zeocarbon are used for preventing anti-fungal microcapsules membrane from being damaged due to friction and impact during mixing, casting, and placing stages of mortar and concrete. Sustainability of Zeolite and Zeocarbon reinforced microcapsules is verified by SEM and HPLC tests. The test results confirm that Zeolite and Zeocarbon are effective in reducing damage of microcapsules in mortar and concrete.

plain mortar with 5 % MC mortar with 15 % MC

(a) 30 days after application of micro-organisms



plain mortar with 5 % MC mortar with 15 % MC

(b) 45 days after first observation of fungus

Fig. 8. Fungus-resistance test results for mortar panel specimens.

2. In the tests for evaluating basic properties of mortar and concrete containing microcapsules, addition of anti-fungal microcapsules increased slump and air content and decreased strength of mortar and concrete. However, overall performances of mortar and concrete containing microcapsules are similar to those of plain mortar and concrete.
3. In the fungal-resistance test of mortar panel specimens, fungus did not grow on the surface of mortar panel containing anti-fungal microcapsules and wide-spread fungi were observed on the surface of plain mortar panel. The anti-fungal effectiveness of mortar containing microcapsules was verified through the comparative test results.
4. In this experimental works for testing physical performance and anti-fungal effectiveness of mortar and concrete containing microcapsules, 5% addition of anti-fungal microcapsules is considered as recommendatory adding rate in perspective of physical performance and economical efficiency. However, since the test results are based on short-term nature of testing program, further experimental works are needed to find the most effective mixing ratio of anti-fungal microcapsules into mortar and concrete.

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References

[1] Ramachandran VS. Concrete admixtures handbook: properties, science, and technology. Noyes Publications; 1995.
[2] University–Industry–Nation Laboratory Joint Research Program Annual Report. Development of anti-fungal and anti-insect concrete and mortar using microcapsule. Korea Ministry of Construction and Transportation Technology Evaluation Office; 2002. p. 01–02.
[3] Robinson RF, Austin CR. Effect of copper-bearing concrete on molds. Indust Eng Chem 1951;43(9):2077–82.
[4] Neville M. Properties of concrete. England: Longman,Harlow; 1996.
[5] ACI 212.3R-91. Chemical admixtures for concrete. ACI manual of concrete practice: Part 1. Materials and general properties of concrete. ACI; 1994.
[6] Do JG, Song H, So HS, Soh YS. Antifungal effects of cement mortars with two types of organic antifungal agents. Cen Con Res 2005;35:371–6.
[7] Alum A, Rashid A, Mobasher B, Abbaszadegan M. Cement-based biocide coatings for controlling algal growth in water distribution canals. Cem Concr Compos 2008;30(9):839–47.
[8] De Muynck W, De Belie N, Verstraete W. Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete. Cem Concr Compos 2009;31(3):163–70.
[9] Park SJ, Lee JR. Preparation and characterization of microcapsule containing lemon oil. J Colloid Interf Sci 2001;241:502–8.
[10] Akay G, Tong L. Preparation of colloidal low-density polyethylene latexes by flow-induced phase inversion emulsification of polymer melt in water. J Colloid Interf Sci 2001;239:342–57.
[11] Vinetsky Y, Magdassi S. Microencapsulation by surfactant–gelatin insoluble complex; effect of pH and surfactant concentration. J Colloid Interf Sci 1997;189:83–91.
[12] Dobashi T, Takenaka M, Yeh FJ. Scattering studies of poly (urea–urethane) microcapsules in suspension. J Colloid Interf Sci 1996;179:640–2.
[13] EEC method for determination of toxicity. Annex to directive 92/69/EEC (OJ No. L383A, 29.12.92). Part B. Method B.1 bis. Acute toxicity (oral).
[14] OECD guideline for testing of chemicals No. 401. Acute oral toxicity; 1987.