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CHARACTERISTICS OF THE TRADITIONAL KOREAN LIME PLASTER AFTER AN ADDITION OF PERILLA OIL

ZNAČILNOSTI TRADICIONALNEGA KOREJSKEGA APNENEGA OMETA Z DODATKOM PERILOVEGA OLJA

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Ancient Korean records indicate that a variety of organic materials (straw, hanji, sticky rice, oil, etc.) used to be added to lime for different purposes, including the preservation and repair of monuments. In this study, aerial lime plaster with perilla oil was produced. Before the sample preparation, a flow test was performed: lime was kneaded at various ratios of mixing water and perilla oil to better understand the physical transformation of the material. After perilla oil was added, the fluidity of the lime putty was decreased, allowing adjustments in the workability. Using the Uigwe as the reference, lime samples with perilla oil were prepared. As even a small amount of perilla oil can cause color changes in the lime material, it is important to control the amount of perilla oil added to the lime putty. Furthermore, the material became resistant to moisture. As freezing and thawing due to the moisture content are the main causes of damage to lime materials, it was believed that the addition of perilla oil can improve their performance. Neutralization tests, μ-CT imaging and an XRD analysis were performed to investigate the carbonation of the lime materials. The test results revealed that when perilla oil was added to the material, the carbonation was delayed; furthermore, the strength of the material decreased initially but increased gradually as the curing progressed. This study suggests that perilla oil can be added to lime to improve its freeze-thaw resistance, which will be helpful in the maintenance of monuments.

Keywords: traditional Korean lime plaster, aerial lime, perilla oil

Starodavni korejski zapisi kažejo, da so se apnu dodajali različni organski materiali (slama, hanji, lepljiv riž, olje, itd.) z različnimi nameni, ki vključujejo tudi ohranjanje in sanacije spomenikov. V predstavljeni študiji so avtorji pripravili apneno testo iz zračnega apna z vsebnostjo perilovega olja. Pred pripravo vzorcev za preiskave, je bil opraviljen test razleza na stresalni mizici, z različnimi deleži vode in perila olja v apnenem testu. Test je pomagal razumeti fizikalno transformacijo materiala. Po dodatku perilovega olja se je razlez apnene mase zmanjšal, kar omogoča prilagajanje obdelovalnosti. Pri pripravi vzorcev apnenega ometa z dodatkom perilovega olja je bila kot primer uporabiljena recepturo iz Uigwe. Vsebnost perilovega olja je bila majhna, saj lahko dodatek tega olja hitro povzroči spremembo barve apnenega testa. Dodatek olja je povzročil odpornost materiala proti vlagi. Ker so cikli zmrzovanja/tajanja pri povečani vlagi glavni vzrok poškodb apnenih materialov, so avtorji ocenili, da lahko dodatek perilovega olja izboljša zmrzlinsko odpornost materiala. Karbonatizacijo apnenih mas je bila preučena z nevtralizacijskimi testi, μ-CT skeniranjem in XRD analizo. Rezultati so pokazali, da dodatek perilovega olja zakasni karbonatizacijo, posledično pa je začetna trdnost materiala manjša. Trdnost materiala se nato povečuje starostjo. Študija je pokazala, da se lahko zaradi izboljšanja zmrzlinske odpornosti materialov z apnenim vezivom, mešanici doda perilovo olje, kar je lahko bilo dobrodošlo pri vzdrževanju spomenikov.

Ključne besede: tradicionalni korejski apneni omet, zračno apno, perilovo olje

1 INTRODUCTION

Lime has been used in various structures in Korea, including buildings, fortresses, graves and mural painting. During the Japanese colonial and modernization era, however, the use of traditional lime in most of the manufacturing decreased and construction methods were discontinued. The use of lime also gradually decreased with the introduction of modern materials such as Portland cement. A wide range of organic materials that used to be added to both domestic and foreign limes to improve their performance were identified. Typically, the research on oil additives in western countries has mostly focused on olive and linseed oils that are commonly used in painting works.[1–5] The moisture absorption of lime greatly decreases after an addition of oil, confirming that oil has a waterproofing effect. However, it must be noted that while the traditional Korean lime is aerial lime, which reacts with atmospheric carbon dioxide and hardens, most studies in western countries are focused on hydraulic lime. Interpreting the results of such a study should therefore account for the differences in lime type.

The National Research Institute of Cultural Heritage constructed the Namhansanseong Mock Yeojaing (Parapet) using aerial lime at the Namhansanseong Emergency Palace in the mountains and monitored it for about three years (**Figure 1**). It was found that the freeze-thaw process of moisture repeatedly occurred during the winter and played a significant role in the damage of the constructed structure.[6] In such cases, cement (a modern material) or waterproofing agents are added to increase the freeze-thaw resistance of the materials. However, these materials have not been evaluated for their stability, and there is a possibility of secondary damage resulting

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Figure 1: Damage to Namhansanseong Mock Yeojang (Parapet) due to freeze-thaw: a) Namhansanseong Yeojang (Parapet) in winter (Gyeonggi Cultural Foundation website), b) detailed photograph of the surface of Namhansanseong Mock Yeojaing (Parapet) damaged by freeze-thaw, c) ice inside the surface crack of Namhansanseong Mock Yeojang (Parapet)

from the incompatibility with the existing raw materials, especially in the case of cement. As the need for environmentally friendly and sustainable materials for monument restoration has increased, re-examining the usefulness of traditional materials has become necessary. In this study, it was determined that oil additives, which are natural products, can enhance the performance of lime, so a literature review on the subject was conducted.

In the Uigwe records,[7] various oil additives were identified, such as perilla oil, sesame oil, myoung oil and tung oil. Perilla oil, which was mentioned the most, is of particular interest. In particular, it is possible to infer information from the records of the 17th century,[8,9] such as addition methods, number of applications and application methods. In this study, perilla oil was added to aerial lime and reproduced in the form of traditional Korean lime plaster based on the contents of the records, and the consequent changes in the properties of the lime materials were investigated.

2 EXPERIMENTAL PART

2.1 Materials

The powder state of slaked lime (B company, Korea) was used as the binder and an edible perilla oil (S company, Korea), commonly used for cooking in Korea, was used as the additive. The perilla oil, used in this study, was produced with the cold-pressed method.

2.2 Flow test

Prior to the creation of the samples, a flow test was performed[10] and the results are in **Table 1**. Lime was kneaded under various ratios of mixing water and perilla oil to better understand the physical transformation of the materials' properties. The proportions of the mixing water were (50, 60 and 70) *w*/% of the lime mass, while those of perilla oil were (1, 3, 5 and 10) *w*/%. The material could not be mixed with a 40 *w*/% proportion of mixing water, not even with an addition of 10 *w*/% perilla oil. The sample produced with 50 *w*/% of mixing water had a very low water content and was destroyed during the demolding process. Accordingly, it was determined that the production of lime plaster samples would be feasible if the proportion of mixing water was 60 *w*/% or more. The flow test indicated that the lime putty that contained 60 *w*/% or 70 *w*/% of mixing water exhibited decreased fluidity as more perilla oil was added. In this case, the larger the content of mixing water, the greater was the decrease in fluidity. It is believed that perilla oil has a greater effect on the lime putty for plastering than on the lime for masonry, because the former needs a higher proportion of mixing water. With the flow test, it was confirmed that the workability of the lime putty could be adjusted with the amount of perilla oil added, and that perilla oil acted as a natural thickener.

Table 1: Flow test results for mixing water and perilla oil

Water (*w*/%)	Perilla oil (*w*/%)				
	–	1	3	5	10
50	107.67	103.10	110.95	107.44	106.81
60	130.98	123.63	123.53	121.49	119.36
70	156.86	146.62	143.81	128.80	127.24
	Average flow value (mm)				

2.3 Sample preparation

The amount of mixing water was set based on the results of the flow test, and the proportions of water and perilla oil were applied based on the lime weight. The compositions of the samples used in the experiment and applied curing conditions are shown in **Table 2**. The experiment was designed to minimize the deviations caused by the conditions other than the additive type, such as lime type, slaking process and aggregate type. Thus, a sample was prepared in the form of plaster with no aggregates (such as sand). The details about the mixing procedure were taken from the reference literature.[11]

The lime putty was molded by filling it in a customized brass mold with dimensions of (20 × 20 × 20) mm and (50 × 50 × 50) mm. In most cases, cube-shaped specimens with a diameter of 20 mm were used, while cube-shaped specimens with a diameter of 50 mm were used for neutralization and freeze-thaw tests. Perilla oil was added in two ways based on the descriptions from

Table 2: Sample proportions and curing compositions

Sample	Lime	Water	Perilla oil	
L	1	0.6	-	Curing for (7, 14, 28, 56 and 91) d Accelerated curing (AC) (7, 14, 28 and 56) d
M0.5	1	0.6	0.5 *w*/% mixed	
M1	1	0.6	1 *w*/% mixed	
M5	1	0.6	5 *w*/% mixed	
B1	1	0.6	1 applied with a hog bristle brush	
B5	1	0.6	5 applied with a hog bristle brush	
B10	1	0.6	10 applied with a hog bristle brush	

*Mixing proportions were based on *w*/%.

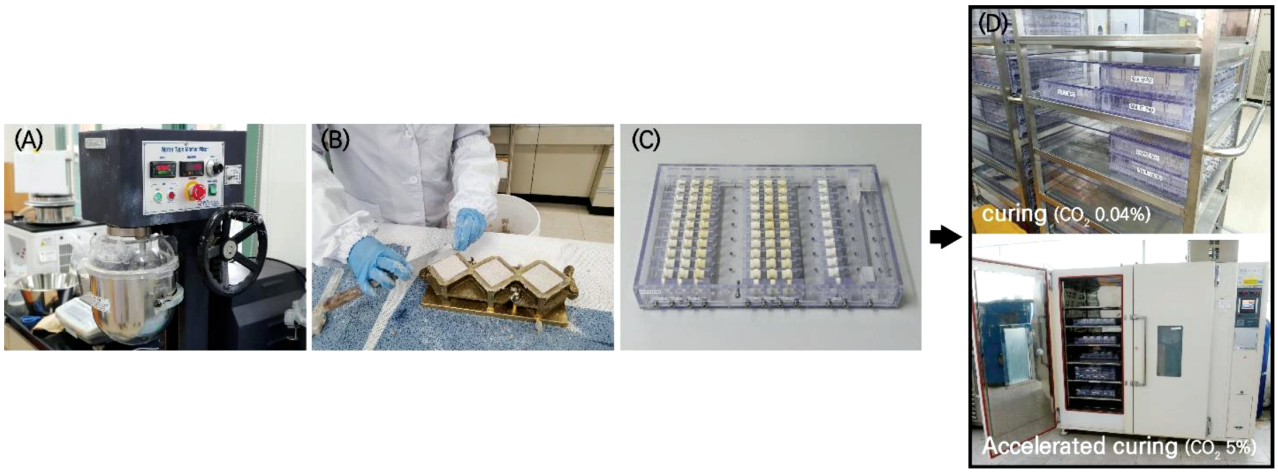

Figure 2: Sample preparation process

the records. The first method involves blending perilla oil with lime and mixing water, and the second involves applying perilla oil onto the surface of a sample. As recommended in the Uigwe, a hog bristle brush was used as the application tool, and the application interval was 1 h.

The manufactured samples were dried at a constant temperature and humidity (23 °C, 50 ± 3 %) and separated from the mold on the fifth day after the manufacture. On the seventh day, the samples were collected and laid on an acrylic holder to be cured under two conditions, curing and accelerated curing. Curing means that the samples are cured with a 0.04 % concentration of CO_2. Accelerated curing (denoted by AC) means the samples are cured with 5 % of CO_2 in a chamber, to check the tendency of long-term curing within a short period of time as well as the curing conditions in an indoor environment (**Figure 2**).

2.4 Analytical methods

To determine the state of the samples, the surfaces were observed under 25× magnification using a portable digital microscope, DG-3 (Scalar, Japan), and the CIE value was obtained using a spectrophotometer (CM-2600d, Konica Minolta, JPN). The standard light source was set at D65, the viewing angle was 10° and the analysis area was ϕ 16 mm. For measuring the chromaticity, the average value of the measurements taken three times at the same location was taken as the final value for our data. The surface contact angle was measured to confirm the moisture resistance. The sessile drop method was applied using Phoenix 300 Touch (SEO), and the contact angle was calculated using Tangent Line Method 2 in the Surfaceware software. In addition, a freeze-thaw test was conducted. In this test, three samples, for which curing was accelerated for 28 d, were used for each composition. The deposition freeze-thaw method was repeatedly applied as a cycle that included 18 h of immersion under water, 3 h of cooling at –20 °C and 3 h of heating at 50 °C. The state of the samples on each cycle was recorded and the ultrasound velocity was measured to compare the changes over time.

A direct method was applied with a measurement distance of 50 mm (sample size) using a Pundit lab (Proceq, Switzerland) device with a probe with a frequency of 54 kHz, voltage of 500 V and a sensitivity of 100×. Three analysis methods were used to determine the degree of carbonation. First, a neutralization test was performed to confirm the discolored area by spraying phenolphthalein on a sample cross-section. Additionally, a μ-CT (XT H 225, Nikon, Japan) analysis was performed to determine the carbonation area without destroying the sample. The imaging conditions were 160 kV, 100 μA and 500 ms. As many as 3015 projection images were collected. The information of the cross-sectional image and internal structure of each axis was obtained using the VG Studio software. The mineral compositions detected in each curing period were also compared through an X-ray diffraction analysis. The

analysis was performed using Cu-K_α rays based on X'Pert3 Powder (PANalytical, UK) with a 2θ value of 33–65°, voltage of 40 kV and current of 30 mA.

To check the strength of the samples, both non-destructive and destructive methods were used. Regarding the non-destructive test method, the Pundit lab device was used in the same manner as for the previous sample subjected to the freeze-thaw test. In this case, the ultrasound velocity measurement was directly performed at a measurement distance of 20 mm (sample size), under a voltage of 500 V, with a sensitivity of 100× using a 54 kHz probe. A UTM (AG-X plus, Shimadzu, Japan) was used for the compression strength measurement with a test rate of 0.5 mm/min and a load cell of 20 000 N.

3 RESULTS AND DISCUSSION

3.1 Physical properties

The longer the curing period, the lower was the brightness of all samples (L*), regardless of the conditions for adding perilla oil. In the case of L, there was a difference of 1.18 between the brightness values of the sample cured for 7 d and the sample that underwent accelerated curing for 56 d without perilla oil, which showed the smallest reduction. When perilla oil was mixed in (M0.5, M1 and M5), differences of 1.80, 3.59, and 3.09 were obtained, respectively. Conversely, when perilla oil was applied (B1, B5 and B10), differences of 2.98, 4.29 and 6.68 were yielded, respectively. Thus, it was confirmed that the range of brightness changes due to prolonged curing was greater when perilla oil was applied. Additionally, samples with a relatively small amount of perilla oil (M0.5, M1, B1 and B5) showed a trend of decreasing redness and increasing yellowness. In contrast, both redness and yellowness increased in the samples containing a high amount of perilla oil (M5 and B10).

Based on the color information for sample L (**Table 3**), the color difference (ΔE) according to the curing period was calculated for each sample. It was found that the color difference increased with the amount of perilla oil added and was greater when perilla oil was applied with the brush compared to that when perilla oil was mixed in. Particularly, sample B10 subjected to accelerated curing for 56 d achieved a value of 21.51, the highest among all the samples.

Table 3: Color differences (ΔE)

	Curing (*d*)					Accelerated curing (AC) (*d*)			
	7	14	28	56	91	7	14	28	56
M0.5	1.41	1.20	1.38	1.52	1.19	3.94	3.83	1.43	2.00
M1	2.87	3.51	3.22	2.46	2.39	9.21	7.08	9.13	8.49
M5	12.48	14.18	14.35	13.99	10.39	14.72	17.68	17.12	17.09
B1	3.19	1.38	2.73	1.57	1.41	1.25	3.95	5.11	6.32
B5	2.47	2.50	5.01	5.37	4.07	8.01	9.51	10.48	7.84
B10	9.95	7.44	7.30	10.17	8.73	13.24	14.39	15.74	21.51

3.2 Water resistance

The moisture absorption properties of the samples differed according to the conditions, under which perilla oil was added (**Table 4**). Sample L was hydrophilic, that is, water was absorbed immediately, before droplets were formed on the surface. The wettability of the surface decreased for the sample that underwent AC for 28 d, and the contact angle increased to 30.80°. For the sample that underwent AC for 56 d, the contact angle was found to be 40.33°. These changes are attributed to the increase in the density. It is presumed that during carbonation the matrix near the surface of a sample became quite dense. Alternatively, the samples into which perilla oil was mixed showed a contact angle of 90° or more in the early stages of curing, and their surface showed hydrophobicity. It was confirmed that the samples to which the oil was applied had lower surface wettability. In particular, samples B1 and B5 showed a high contact angle of 110° or more. The contact angle for B10, to which perilla oil was applied for the maximum number of times, was 89.22°, the lowest among all the samples with added perilla oil.

As the curing time increased, a difference in the surface contact angle was observed in the early stages of curing. After curing for 91 d, the contact angles of M0.5, M1 and M5, mixed with perilla oil, decreased to 90° or less. In addition, the contact angle repeatedly increased or decreased when the sample was exposed to accelerated curing, but no specific pattern was observed. Meanwhile, B1, B5 and B10 with applied perilla oil showed a slight decrease in contact angles, but their values re-

Table 4: Contact angle (°) measurement results by curing

	Curing (d)					Accelerated curing (AC) (d)			
	7	14	28	56	91	7	14	28	56
L	–	–	–	–	–	–	–	30.80	40.33
M0.5	104.43	95.32	102.81	88.45	84.26	83.63	110.39	101.44	85.96
M1	106.93	97.00	105.10	95.53	89.72	100.4	108.59	104.83	100.84
M5	105.32	98.14	90.17	95.51	84.71	106.79	106.56	104.57	99.33
B1	111.23	106.25	110.86	91.88	107.43	94.65	106.18	102.85	109.92
B5	115.62	100.79	95.82	95.80	97.37	109.33	105.82	105.19	105.43
B10	89.22	101.72	111.42	107.04	94.37	117.41	104.46	103.65	99.37

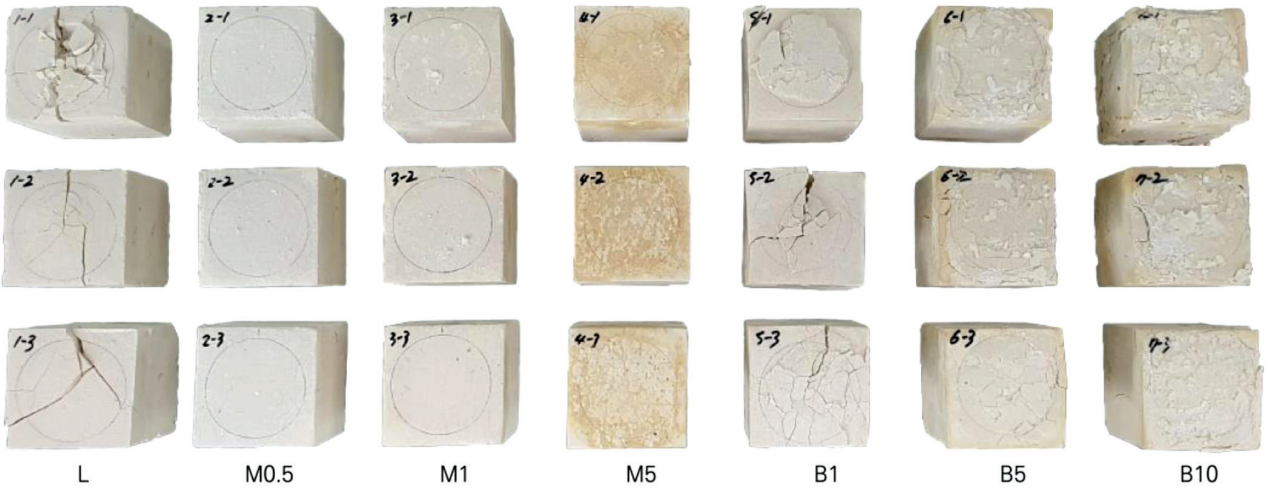

Figure 3: Freeze-thaw test results after 3rd cycle

mained at 90° or more. Particularly, the contact angle of B10 increased from 89.22° at the start of curing to 94.37°. The contact angle of the samples with perilla oil applied continued to rise after the 7th day of AC. Among the samples subjected to accelerated carbonation for 56 d, the final contact angle of the samples with perilla oil (M0.5, M1, M5, B1, B5, B10) was higher than that of sample L. Therefore, it can be determined that the samples to which perilla oil was applied have better surface water resistance.

Each sample subjected to accelerated curing for 28 d before the freeze-thaw test showed no identifiable physical damage. However, discoloration due to the addition of perilla oil was noticed in B5, B10 and M5. Sample M5 was especially dark in color and had a non-uniform surface compared to the other samples. The state of the sample was evaluated for the first time after the 3rd freeze-thaw cycle (**Figure 3**). When mixed with perilla oil, samples (M0.5, M1, M5) were generally in good condition. The samples under the condition in which perilla oil was not added (L) or perilla oil was merely applied to the surface (B1, B5, B10) were physically damaged. The samples in these cases were destroyed by cracks, but detailed patterns of the cracks differed. Both sample L and B1 had a large structural crack on the surface. However, samples B5 and B10 had relatively small and shallow cracks. Additionally, rather than having the scaling peeled by frost, as was the case with samples L and B1, the surfaces were separated into chunks. Therefore, some freeze-thaw effects after the addition of perilla oil were confirmed.

Damage was also observed on the surface of the samples with perilla oil mixed in after the 5th cycle of freezing and thawing. Here, it was confirmed that sample M5, which had the largest amount of perilla oil added, showed more severe damage than M0.5 and M1. The results of the surface observation revealed that pulverization resulted in cracks. At this point, similar to the samples to which perilla oil was applied, samples mixed with perilla oil showed a damage pattern, indicating that the surface was pulverized and peeled off, which differed from the perilla oil-free sample L. The damage to all the samples intensified during the 7th freeze-thaw cycle. As the surfaces were powdered and destroyed, all the samples showed the same patterns, and their corners fell off. Using a visual and portable microscope, the damage to M5 was determined to be the most significant. In all the samples, physical damage such as surface exfoliation, powdering, falls and cracks increased after the 10th freeze-thaw cycle. In particular, sample M5 was on the verge of destruction due to the cracks.

Table 5 illustrates the changes in the physical properties obtained with ultrasound velocity measurements for different numbers of cycles. In the case of the samples for which accelerated curing was performed for 28 d before the freeze-thaw test, the ultrasound velocity for B1 was 2088 m/s (the highest), while that for sample L was 2085 m/s, which was almost the same as for B1. In contrast, the samples with a relatively large amount of perilla oil added showed an ultrasound velocity range of 1128–1567 m/s.

Table 5: Ultrasound velocity of the samples by cycle

Sample	Ultrasound velocity (m/s)				
	0 cycle	3rd cycle	5th cycle	7th cycle	10th cycle
L	2085	2728	–	–	–
M0.5	1514	1251	1313	1141	1073
M1	1567	1756	1725	1512	1070
M5	1488	1531	1535	1514	1360
B1	2088	1699	–	–	–
B5	1373	795	–	–	–
B10	1128	479	–	–	–

After the 3rd cycle of the freeze-thaw test, most of the samples containing perilla oil had a reduced ultrasound value, but M1 and M5 had slightly increased ultrasound values. Here, sample L showed an increase of 643 m/s in the ultrasound velocity despite substantial physical dam-

age. It is difficult to interpret this increase as an increase in the physical properties of the sample. The ultrasound velocity of B1, B5 and B10 decreased by 389 m/s, 578 m/s and 649 m/s, respectively. As described above, both the samples to which perilla oil was not added and the samples to which it was scarcely applied were significantly damaged by the 3rd cycle. Consequently, it was determined that further measurements of the ultrasound velocity would be difficult.

The results of the ultrasound velocity measurements of the samples mixed with perilla oil after the 5th cycles of freeze-thaw showed that the average ultrasound velocity of M0.5 and M5 increased, whereas that of M1 decreased. In spite of the differences in the conditions, there is very little change in the physical properties evidenced by the deviation in the ultrasound velocity. After the 7th cycles of freeze-thaw, the ultrasound velocity started to differ. First, the ultrasound velocity of M0.5 decreased by 173 m/s compared to the previous cycle, while that of M1 and M5 decreased by 213 m/s and 21 m/s, respectively. Samples M0.5 and M1 exhibited values considerably different from their previous cycle, while M5 with the highest amount of mixed perilla oil showed a smaller difference. All the samples exhibited a decrease in the ultrasound velocity after the 10th freeze-thaw cycle. For M0.5, M1 and M5, the ultrasound velocity decreased by 68 m/s, 442 m/s and 154 m/s, respectively. Thus, we determined that M5 had the highest ultrasound velocity. At this point, signs of physical damage were discovered in the samples, so the freeze-thaw experiment was ended.

3.3 Carbonation properties

The neutralization test is a traditional technique for measuring the progress of carbonation in cement and concrete. As lime also includes calcium oxide, a neutralization test can be applied. When a 1 % phenolphthalein solution is sprayed on the cross-section after cutting the center of the sample's Z-axis, the color of the region containing alkalinity changes depending on the pH of the sample. Thus, the degree of the carbonation progress can be determined by checking the discolored region (**Figure 4**).

Until the 56th day of indoor curing, no color change appeared on the cross-section of L, but color differences appeared outside the sample after the 91st day of indoor curing. As the accelerated curing period increased, the area with no color change increased, indicating that carbonation occurred. Unlike L, samples containing perilla

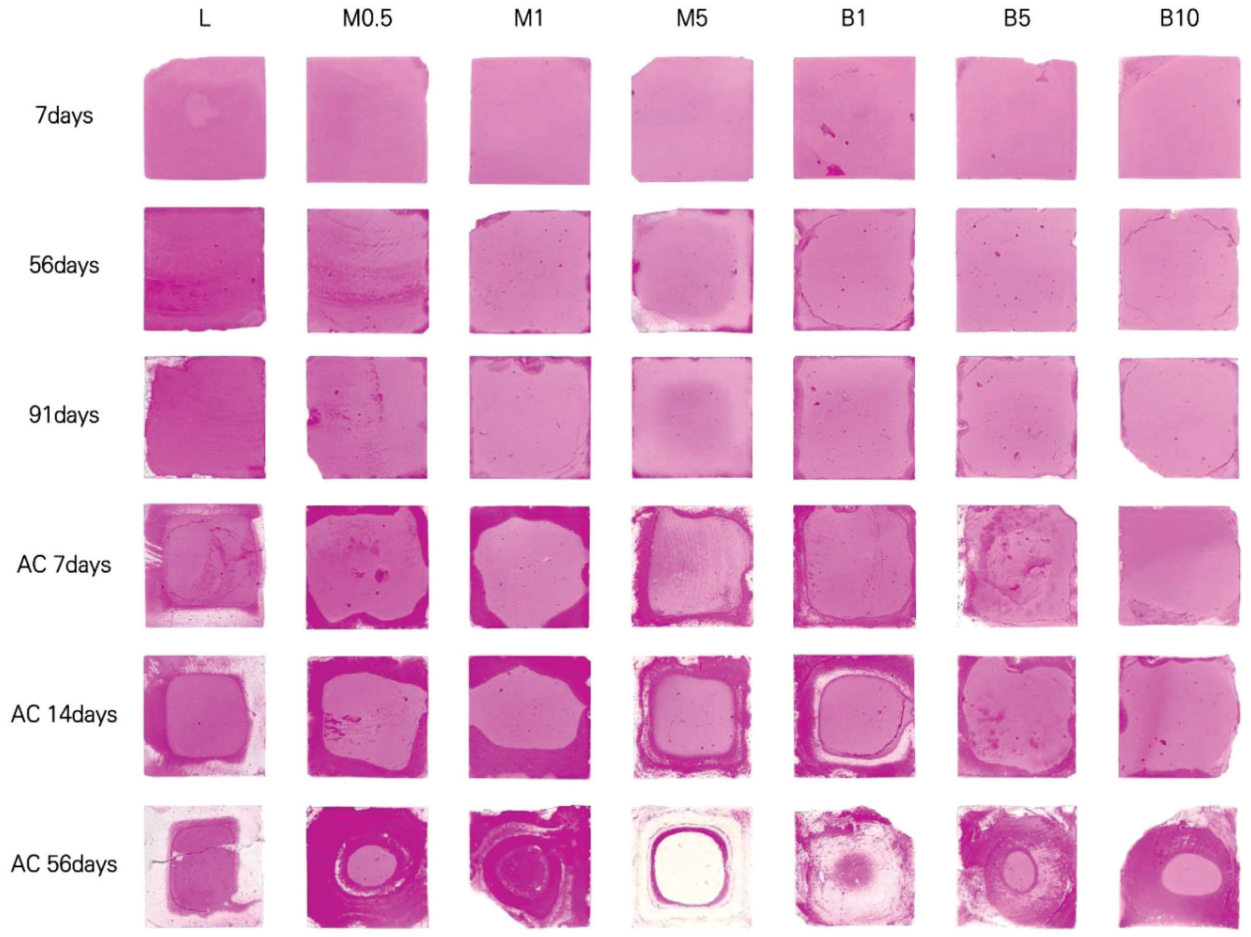

Figure 4: Neutralization test results (sample size of (50 × 50 × 50) mm)

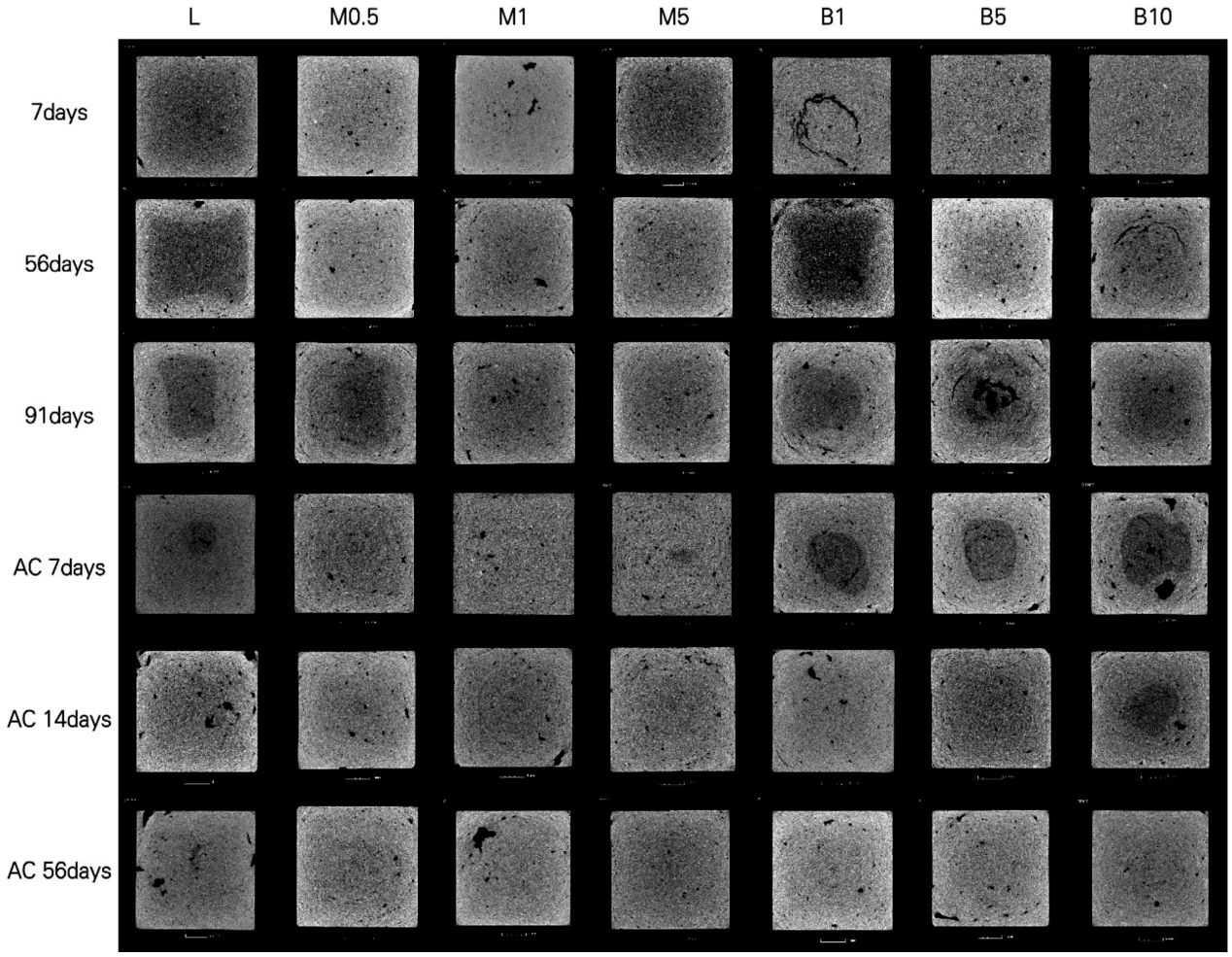

Figure 5: μ-CT analysis images (sample size of (20 × 20 × 20) mm)

oil failed to clearly show any discolored areas. Depending on the sample, there may be a difference in the shade of discoloration, or a ring-shaped pattern may appear in a liesegang pattern.[12] As a result, the neutralization test could not clearly identify the carbonated areas of the lime plaster samples containing perilla oil.

Furthermore, it is possible to obtain a 3D voxel image and a cross-sectional image without destroying the samples. The 2D images from **Figure 5** were acquired with a μ-CT analysis where we observed the samples along the Z-axis. These μ-CT images have different gray values depending on the density of the materials. The areas with a low gray value (a relatively dark part) usually have a lower density, which means that there are gaps in the samples or lime materials that have not been carbonated yet. However, a region with a high gray value (a relatively bright part) denotes a dense part, such as a lime material that has undergone carbonation. In this way, the carbonation region can be estimated by measuring the shade difference.

From the 28th day of the indoor curing onwards, the carbonation of sample L can be seen progressing around the outside shading. As the carbonation region gradually expands throughout the curing period, no shade difference is detected on the cross-sections of the samples on the 14th day of accelerated carbonation, and carbonation might therefore be considered complete. The M0.5 cured for 91 d has a slight shading difference at the center, but the samples mixed with perilla oil have areas of ambiguous shading. When perilla oil is applied, samples show a more obvious shade difference than the samples with mixed perilla oil. Nevertheless, the area where carbonation has not yet been completed is wider than that of sample L. The carbonation area of B5 is unclear on the 91st day of indoor curing, but it becomes distinct on the 7th day of accelerated curing, and there is no shade difference on the cross-section on the 14th day of accelerated curing. A noticeable shade difference is also evident on sample B10 from the 7th day of accelerated curing onwards. In contrast to the other conditions, the area where carbonation has not progressed is wider. It is therefore confirmed that the carbonation of B10 was occurring until the 14th day of indoor curing and 28th day of accelerated curing. According to the μ-CT analysis results, carbonation is delayed when increasing amounts of perilla

oil are applied. In the case of mixed perilla oil, it is difficult to locate carbonation areas on the CT images.

The (20 × 20 × 20) mm samples used for the μ-CT analysis were pulverized, and an X-ray diffraction analysis was performed on them. The main minerals detected in all the samples include portlandite, which is calcium hydroxide ($Ca(OH)_2$), and calcite, a calcium carbonate ($CaCO_3$). Calcium hydroxide is converted into calcium carbonate in the process of carbonation by reacting with carbon dioxide in the atmosphere. Therefore, it is possible to determine whether the material is carbonized based on the changing diffraction pattern (**Figure 6**).

The portlandite peak was mostly observed for sample L on the 7th day of indoor curing. From the 14th day of indoor curing onwards, the frequency and intensity of the calcite peak began to increase. From the 91st day of indoor curing onward, its diffraction peak became more dominant than the portlandite peak. The longer the curing period, the sharper the peak of the calcite becomes, while the portlandite peak tends to gradually flatten, indicating that carbonation is in progress.

Sample M0.5 shows an increasing pattern of the calcite peak after the 14th day of curing, and its diffraction pattern based on the curing period is almost identical to that of sample L. On the 7th day of accelerated carbonation, the portlandite peaks became flatter, while the calcite peaks became sharper. The portlandite peaks of M1 were mostly detected in the early stages of curing. The frequency of the calcite peaks began to increase on the 14th day of indoor curing, but they were weaker than those of M0.5, which was cured during the same time period. As the curing period was prolonged, the portlandite peak gradually became planar, and the diffraction pattern with sharp calcite peaks is similar to that obtained under the previous condition. In the early stages of curing, M5 also exhibited the same diffraction pattern. In this case, however, the diffraction peaks of calcite were difficult to detect. That is, calcite peaks appeared weakly on the 28th day of curing, but the portlandite peaks were dominant until the 91st day of indoor curing. A calcite peak was clearly visible on the 7th day of accelerated curing along with a decrease in the portlandite peak. It can be assumed from this diffraction pattern that carbonation reactions are delayed as the amount of perilla oil added increases.

The diffraction pattern of sample B1, which does not contain much perilla oil, is almost identical to that of sample L. From the 14th day of indoor curing, the calcite peak amplitude began to increase, and its diffraction peak became more dominant than the portlandite peak by the 91st day of indoor curing, similar to oil-free conditions. The diffraction patterns of B5 were similar to those of L and B1 during the early stages of curing. However, on the 91st day of indoor curing, the calcite diffraction peak was weaker than those of L and B1 during the same period, and portlandite still dominated. The portlandite peak became flat, and the calcite peak became sharp only after accelerated curing was performed for 7 days. From the 7th to the 14th day of indoor curing, B10 exhibited the same diffraction pattern, with

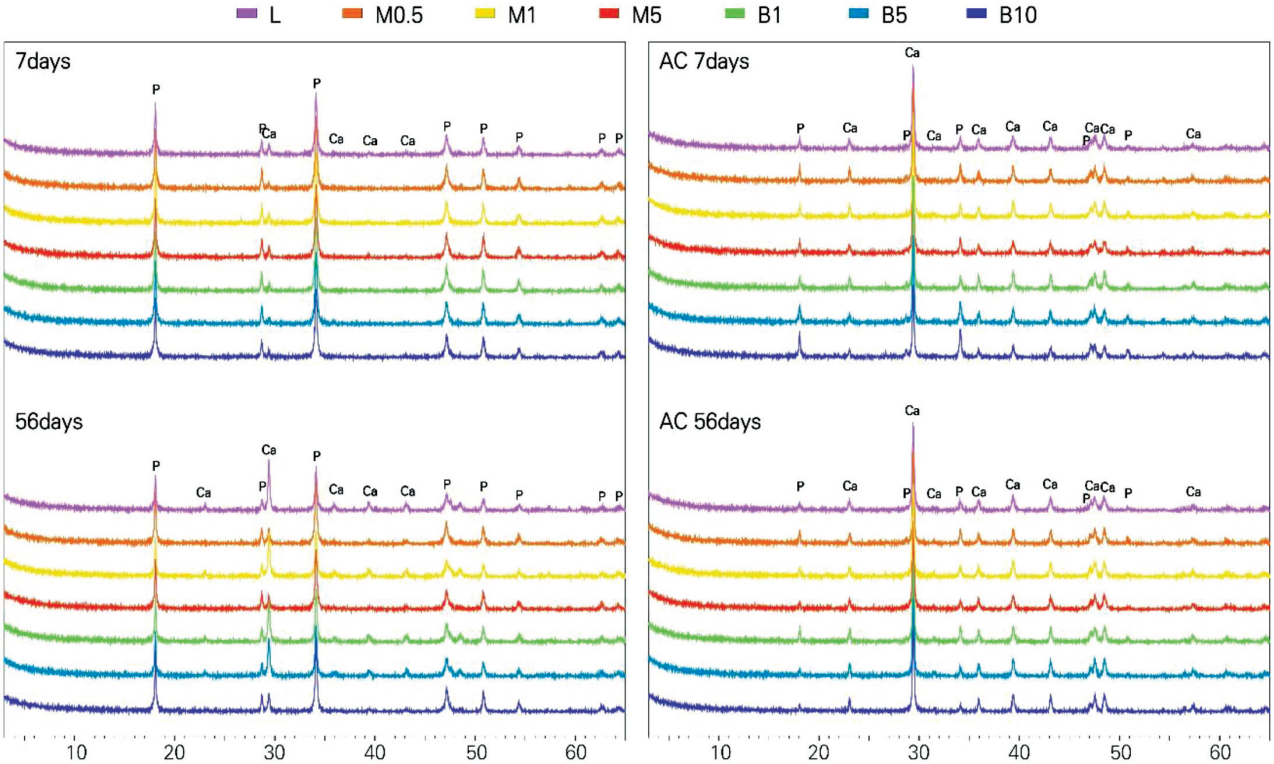

Figure 6: XRD analysis results (P – portlandite, Ca – calcite)

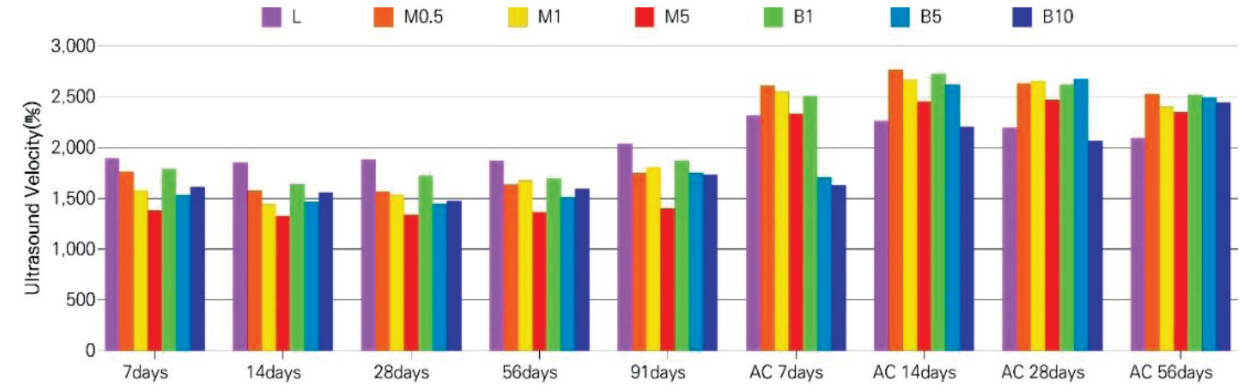

Figure 7: Ultrasound velocity (m/s)

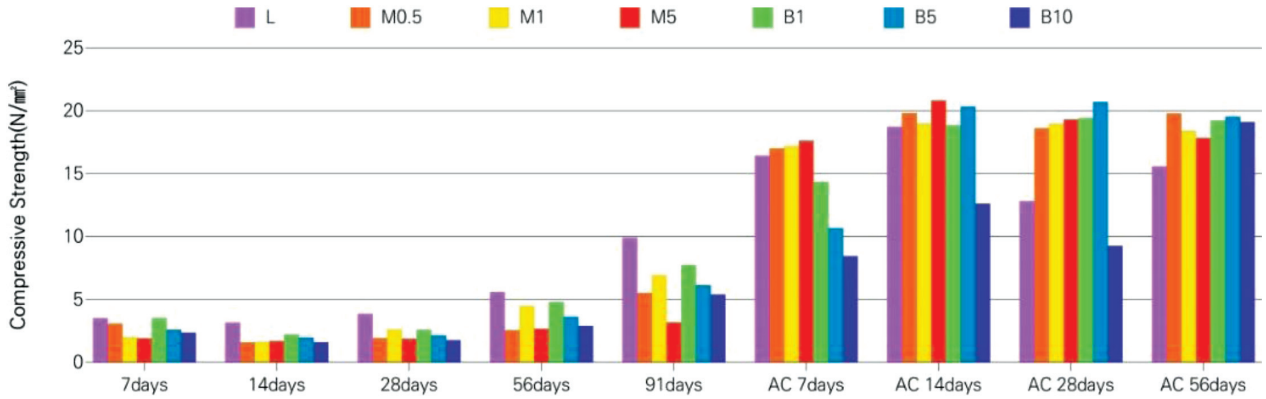

Figure 8: Compressive strength (N/mm^2)

portlandite being dominant. Under the conditions in which a small amount of perilla oil was added (L, M0.5, M1, B1), it was more difficult to confirm the calcite diffraction peak. Calcite was only slightly detectable after the 28th day of indoor curing. As late as the 91st day of indoor curing, the portlandite peak was still dominant. The calcite peak was dominant only from the 7th day of accelerated curing onwards. In this way, the carbonation delay due to perilla oil was also observed in the diffraction pattern of B10 to which oil was applied most frequently.

3.4 Strength properties

The strength of the lime-plaster samples with respect to the method of adding perilla oil and the curing period was compared with the ultrasound velocity measurements (non-destructive analysis) and compressive strength measurements (destructive analysis). The ultrasound velocity measurement results revealed that the strength of the samples to which perilla oil was not added, or only a small amount was added, was relatively high (**Figure 7**). The increase in the strength was quickly detected for the samples into which the oil was mixed, while the increase in the strength for the samples to which perilla oil was only applied onto the surface was delayed as the number of times the perilla oil was applied increased. Furthermore, the strength of the sample without perilla oil was higher for about three months after the sample preparation. However, the longer the curing period, the higher was the strength in the case of included perilla oil. Due to the delay in the increase in the strength, B10 required a long curing period before it reached a physical strength comparable to that of the samples under other conditions. The compressive strength of the samples was determined through a destructive analysis of the samples, for which the ultrasound velocity was measured (**Figure 8**). When the compressive strength was measured, the increase in the strength of the samples without perilla oil, or with small amounts of perilla oil, was high. The increase in the strength was low when perilla oil was applied compared to when a small amount, or no amount, of perilla oil was added. Accordingly, it can be determined that the ultrasound velocity and compressive strength measurements show similar trends.

The linear model confirmed the correlation between the non-destructive analysis (ultrasound velocity measurement) and destructive analysis (compressive strength measurement), like in **Figure 9**. The coefficient of determination (R^2) of the condition in which perilla oil was not added was 0.78, representing the lowest value among all the conditions. The conditions in which perilla oil was mixed into the samples showed a correlation of 0.96 or more, and the conditions in which perilla oil was just applied to the surface also showed a coefficient of deter-

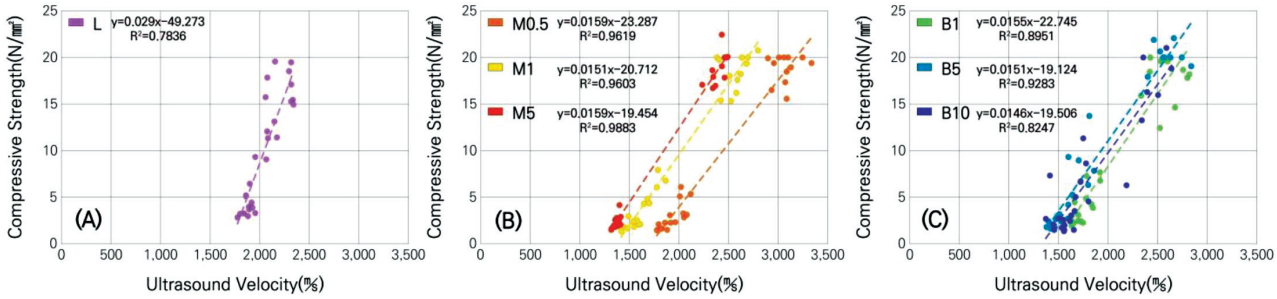

Figure 9: Strength correlation of lime plasters based on ultrasound velocity and compressive strength measurement: a) without perilla oil, b) with perilla oil mixed, c) with perilla oil applied

mination of 0.82–0.98. Thus, it was confirmed that the two measurements used for the strength analysis of the lime plaster samples containing perilla oil exhibited high reproducibility.

4 CONCLUSIONS

In this study, perilla oil was added to aerial lime based on the records of the Korean Uigwe, and the resulting characteristics were verified. In the flow test, the fluidity of the material (lime putty) decreased as the amount of perilla oil added increased. Subsequently, the fluidity decreased significantly as the moisture content in the lime putty increased. The fluidity may have decreased because the absorption ratio of lime decreased and perilla oil acted as a natural thickener. The thickener suppresses material separation and can be used to adjust the flow of a material with only a small amount added. Therefore, an addition of perilla oil will most likely increase workability. The brightness of the samples produced by adding perilla oil decreased as the curing period increased; and the tendency of the redness or yellowness to increase or decrease appeared to differ, depending on the method of adding perilla oil to the samples (mixed vs. applied). The samples with added perilla oil showed more color difference compared to those without perilla oil. Hence, if perilla oil is added to lime in a construction field, care should be taken to prevent excessive discoloration. Above all, as previous studies indicated, the moisture absorption properties of the aerial lime plaster samples decreased with an addition of perilla oil.

In addition, water resistance was confirmed via contact-angle measurements. Water resistance was better when perilla oil was applied than when it was mixed. However, the freeze-thaw test revealed a difference in the destruction pattern between the samples containing perilla oil and those without it, whereas the samples mixed with perilla oil were more durable. This is because the samples to which perilla oil was applied were waterproof only on the surface where the oil was applied.[13,14] In addition, the carbonation of lime was delayed when perilla oil was added. Consequently, in the early stages of curing, the samples without perilla oil showed the greatest strength. As curing progressed, the strength increased significantly. Here, the strength of the samples was estimated by measuring ultrasound velocity and compressive strength, and a high correlation between those two measurement methods was confirmed for particular samples.

Overall, this study demonstrated that it is possible to enhance the performance of traditional lime by adding perilla oil to it, which leads to improved workability and water resistance. The lime used for monuments can be severely damaged during winter or in mountainous areas. In this regard, lime with water resistance and freeze-thaw resistance can be advantageous for the maintenance purposes. Hence, by adding a small amount of perilla oil during a construction using lime mortar, the damage caused by freezing and thawing in winter can be minimized. However, the study has some limitations. It is still necessary to examine the perilla oil applying method, which made the material highly waterproof only when the construction surface was flat, such as wall plaster. Further, perilla oil applied in the field should be studied with regard to mortar samples mixed with aggregates, such as sand, via additional experiments. It is also important to examine the performance of lime when various organic additives identified in the Uigwe are added in combination with perilla oil.

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5 REFERENCES

[1] C. Nunes, Z. Slížková, D. Křivánková, Lime-based mortars with linseed oil: sodium chloride resistance assessment and characterization of the degraded material, Periodico di Mineralogia, 82 (**2013**) 3, 411–427, doi:10.2451/2013PM0024

[2] C. Nunes, Z. Slížková, Hydrophobic lime based mortars with linseed oil: Characterization and durability assessment, Cement and Concrete Research, 61–62 (**2014**), 28–39, doi:10.1016/j.cemconres.2014.03.011

[3] C. Nunes, P. Mácová, D. Frankeová, R. Ševčík, A. Viani, Influence of linseed oil on the microstructure and composition of lime and lime-metakaolin pastes after a long curing time, Construction and

Building Materials, 189 (**2018**) 20, 787–796, doi:10.1016/j.conbuildmat.2018.09.054

[4] L. Ventolà, M. Vendrell, P. Giraldez, L. Merino, Traditional organic additives improve lime mortars: New old materials for restoration and building natural stone fabrics, Construction and Building Materials, 25 (**2011**) 8, 3313–3318, doi:10.1016/j.conbuildmat.2011.03.020

[5] P. Zhao, M. D. Jackson, Y. Zhang, G. Li, P. J. M. Monteiro, L. Yang, Material characteristics of ancient Chinese lime binder and experimental reproductions with organic admixtures, Construction and Building Materials, 84 (**2015**) 1, 477–488, doi:10.1016/j.conbuildmat.2015.03.065

[6] National Research Institute of Cultural Heritage, Trial applications of traditional lime mortar, 2020, 6–327

[7] Royal Construction Projects (Repairs) of Oegyujanggak Uigwe: The Royal Protocols of the Joseon Dynasty

[8] Uigwe for Renovating the Changdeokgung Palace and Changgyeonggung Palace, 1652, 177, 223

[9] Uigwe for Installing the Royal Coffin Hall and Spirit Hall of King Hyojong, 1659, 1091

[10] KS L 5111: Flow table for use in tests of hydraulic cement, 2017

[11] KS L 5109: Practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency, 2017

[12] C. Rodriguez-Navarro, O. Cazalla, E. Sebastian, Liesegang pattern development in carbonating traditional lime mortars, Materials Science, 458 (**2002**), 2261–2273, doi:10.1098/rspa.2002.0975

[13] S. H. Kang, S. Y. Kang, A preliminary study on the effect of perilla oil additive to traditional lime based plaster, Proceedings of the annual conference of the Architectural Institute of Korea, 2020, 538

[14] National Research Institute of Cultural Heritage, Value and Future of Traditional Materials, 2020, 42–48