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Physical properties of natural hydraulic lime mixed with biodegradable organic admixture

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The physical properties of natural hydraulic lime were improved through mixing biodegradable organic admixtures with natural hydraulic lime manufactured by using low grade limestone produced in Korea in order to extend the scope of application. The experiment was conducted according to the EU standards. A total of four organic admixtures (potato starch, corn starch, cellulose, and gelatin) were used to investigate the properties depending on the kind of organic admixture and the changes in the properties depending on the amount of mixed organic admixtures. The results of the study showed that the initial compressive strength on 7 days was increased and the setting time was shortened by the mixing of the organic admixtures. Considering the physical properties such as compression strength, setting, air content, and soundness according to the EU standards, the best physical properties were obtained when corn starch, one of the four organic mixtures, was mixed at a mixing ratio of 1.0%.

Key words: Natural hydraulic lime (NHL), Biodegradable organic admixture, Low-grade limestone, Physical property, Compressive strength.

Introduction

Natural hydraulic lime (NHL), which is an environment-friendly building material produced by using low grade limestone, may be stably used under unfavorable environmental conditions. This is because NHL has hazardous substance absorptivity, antifungal properties, and constant temperature and humidity properties. In addition, NHL may be used as a concrete aggregate and soil or water stabilizer, even after being discarded, and it does not make any substances harmful to the environment when it is stacked. Hence, NHL is an excellent resource recirculation material [1-3]. NHL may be used variously as a finishing material, an interior or cladding material, and as a binder depending on the mortar or paste mixing conditions and application methods. However, the physical properties sometimes need to be modified for actual applications due to the low compressive strength and long setting time [4, 5]. The EU standards do not regulate the scope of admixtures for NHL. Instead, they allow the mixing of various admixtures based on need, regardless of organic or inorganic admixtures [6].

In the modern building material market requiring material to be environment-friendly, biodegradable admixtures are drawing attentions as highly environment-friendly alternative materials to prevent environment pollution due to their high applicability. The scope of biodegradable environment-friendly materials is very wide, as it includes plant resources (plant stems, vegetable oils, waste plant cellulose, wood substances), microorganisms, marine organism resources, and animal resources (blood, animal oils, animal fur) [7, 8]. According to previous studies, the greatest advantage of mixing an organic admixture with an ordinary Portland cement (OPC) mortar or concrete is that the organic admixture may function as a water-reducing agent without a harmful substance. Other advantages include enhanced strength, shortened setting time, increased viscosity, and increased moisture retention capacity [8-11]. Although organic admixtures have not been introduced as generally applied materials until now due to the high price and low technological level, the demand for organic admixtures as environment-friendly admixtures is increasing in the market, as the product quality is increasing and the soundness of physical properties is secured due to the recent technological development.

In the present study, the applicability of biodegradable organic admixtures to NHL, which is an environment-friendly building material, was experimentally investigated. The physical properties of the organic admixtures were also evaluated to verify whether the requirements of the EU standards are satisfied.

Experimental Method

Starting materials

The NHL was prepared by using low grade limestone

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Table 1. Chemical compositions of low-grade limestone (%, by weight).

MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3
1.32	3.04	13.8	42.8	0.98

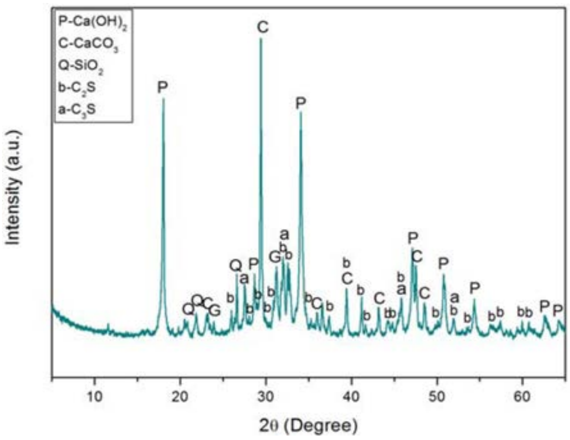

Fig. 1. XRD pattern of local Korean NHL.

produced in Korea. Table 1 shows the results of chemically analyzing the low grade limestone produced in Korea. The content of the components contributing to the formation of hydraulic mineral phases was about 13% of SiO_2, about 3% of Al_2O_3, and about 42% of CaO, indicating that NHL could be easily prepared from the limestone. For the calcination of the raw materials, the low grade limestone was crushed into pieces of 10 to 20 mm. The calcination was performed at 1250 °C for two hours. Afterwards, hydration, drying, and pulverization were performed to produce the final product. Fig. 1 shows the XRD analysis results of the final product's mineral phases. The analysis showed that the main mineral phases were $Ca(OH)_2$, $CaCO_3$, SiO_2, C_2S, and C_3S, which were similar to those of general NHL. The coexistence of $Ca(OH)_2$, which contributes to carbonation, with C_2S and C_3S, which are hydraulic mineral phases, indicates that the durability of a hardened body may be enhanced by a complex hardening mechanism including carbonation and hydration.

Four reagent-grade admixtures of potato starch, corn starch, gelatin, and cellulose produced by D company in Korea were used in the experiments.

Test method

The experiment was conducted to investigate the physical properties of NHL mixed with organic admixtures according to the BS EN 459-2 : 2015 standards. Each of the physical properties was measured by the following methods.

The flow of NHL mortar was evaluated based on the kind of organic admixtures and their contents. The ratio of water was 70% in the preparation of the mortar. The mortar was compacted on a flow table mold in two layers immediately after it was prepared, and then the top surface was leveled. After the form was removed by lifting up the flow table mold, tamping was performed 15 times to spread the mortar, of which the bottom diameter was them measured.

Table 2. Experimental conditions of NHL mortar with types of organic admixture.

Base sample	NHL
Organic admixture	potato starch, corn starch, cellulose, gelatin
Mixing ratio (%, by weight)	0.5
Water ratio (%, by weight)	70
Curing condition	temperature 20 °C, relative humidity 95%
Curing (days)	7, 28

Table 3. Experimental conditions of NHL mortar with contents of corn starch.

Base sample	NHL
Organic admixture	corn starch
Mixing ratio (%, by weight)	0, 0.5, 1.0, 1.5
Water ratio (%, by weight)	70
Curing condition	temperature 20 °C, relative humidity 95%
Curing (days)	7, 28

The strength depending on the kind of admixtures and the changes in strength depending on the content of one representative organic admixture (corn starch) were investigated. After the first pre-mixing of each organic admixture with NHL, the mortar was prepared at a ratio of NHL (+organic admixture) : sand : water = 1 (+organic admixture) : 3 : 0.7. The prepared mortar was cured at a temperature of 20 °C and a relative humidity of 95%, and the compressive strength of the cured mortar was measured on 7 days and 28 days. The loading speed was 144 kN/min in the process of measuring the compressive strength. Tables 2 and 3 show the mortar preparation conditions depending on the kind of organic admixtures and the mixed sand ratio.

A setting time test was performed by using a Vicat apparatus. The water ratio was determined to make the distance between the base plate and the needle be (6 ± 2) mm. The paste was cured for 30 minutes in a constant temperature and humidity chamber at a temperature of 20 °C and a relative humidity of 95 %. The initial setting time was measured in an interval ranging from 10 to 30 minutes, and the final set ting time was measured on the bottom surface of the specimen by overturning the mold after completing the initial setting.

The measured sample was prepared in the form of a disk having a diameter of 50 mm and a height of 10 mm, and then cured for 24 hrs. After the curing, the sample was steamed for 180 minutes with a steam temperature of 90 °C. The ratio of horizontal and longitudinal length changes was also measured. Formula 1 is the equation for calculating the length change ratios. In Formula 1, D_e denotes the sample diameter after steaming, and D_i denotes the sample diameter before steaming.

$$\text{Soundness (mm)} = (D_e - D_i) \quad (1)$$

The air content in the mortar before curing was measured by air indentation. The water ratio in the mortar preparation was set to make the flow be about (165 ± 3) mm. The mortar before curing was compacted in three layers in the measuring apparatus mold, and then the apparatus covering was attached. The measurement was performed by a watertight method where water is injected to the space between the mortar and the covering. The air content was measured by injecting air.

Results

The change in the NHL mortar flow depending on the addition of organic admixtures was verified, and the applicability of the organic admixtures as a water-reducing agent was reviewed. Fig. 2 shows the results of the flow measurement of the NHL mortar before curing depending on the addition of organic admixtures [11]. The flow test result showed that the flow of the mortar decreased from adding organic admixtures in comparison with the plain sample. The same decrease in flow was found regardless of the kind of organic admixtures. Thus, the applicability of the organic admixtures as a natural water-reduction agent for NHL was found to be low. Among the samples mixed with organic admixtures, the samples mixed with potato starch and corn starch showed a flow of 154 mm and 155 mm, respectively, indicating that the flow of starch-based admixtures was better. Cellulose usually has a linear molecular structure, but starch has a complex network molecular structure consisting of amylopectin, and thus includes regular hydroxide bonds [8, 10]. Therefore, the moisture adsorption and water retention capability of the starch-based admixture is higher due to the OH^- functional group than those of other organic admixtures, resulting in better flow [8, 12].

Fig. 3 shows the results of the compressive strength measurements of the NHL depending on the addition of organic admixtures. In all the mortar samples to which the organic admixtures were added, the initial strength was higher than that of the plain sample. The compressive strength measured on 7 days was 2 MPa, which is a value that corresponds to the NHL 5 of the NHL classification according to the EU standards.

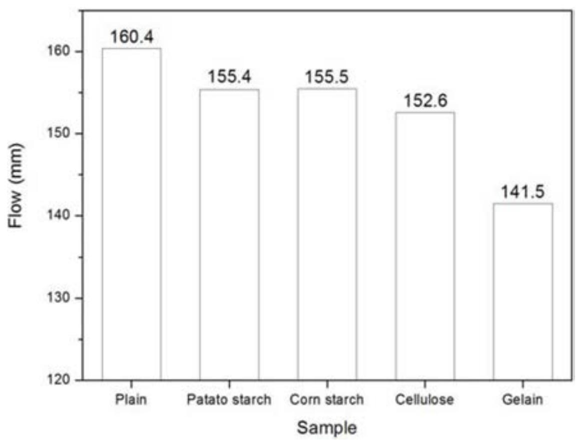

Fig. 2. Mean flow results of mortar with types of organic admixtures.

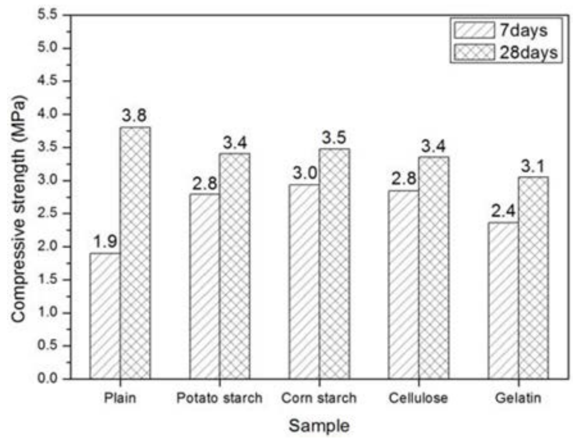

Fig. 3. Compressive strength of mortar with types of organic admixtures.

However, the compressive strength measured on 28 days was the highest in the plain sample, but the difference was not significant with other mortar samples mixed with organic admixtures.

NHL has a long-term hardening mechanism where carbonation and hydration occur complexly, and thus the substantial increase of durability gradually took place after 28 days and the hardened body durability was slightly low at an early curing [2, 13]. The initial enhancement of strength at an early curing may be because the durability increased as the bond between NHL and the aggregate particles was strengthened by the gelation of the added organic admixtures. With regards to the strength at a long curing, the attachment of the organic admixture gel to the NHL particle surface rather inhibited the hydration and carbonation, resulting in a slightly lower strength-enhancing effect [8]. Therefore, further studies may need to be conducted regarding the physical properties after 28 days. The determination of the optimal mixing ratio that does not hurt the original physical properties of NHL seems to also be very important.

The NHL suitability evaluation according to the EU

Table 4. Physical properties of hydraulic lime containing organic admixture.

Sample	Air content (%)	Soundness (mm)	Setting time	
			Initial	final
Plain	2.2	−0.2	18 h	23 h
Potato starch	2.9	–	6 h	8 h
Corn starch	2.7	–	7 h	10 h
Cellulose	2.9	–	11 h	14 h
Gelatin	3.8	–	3 h 30 min	7 h

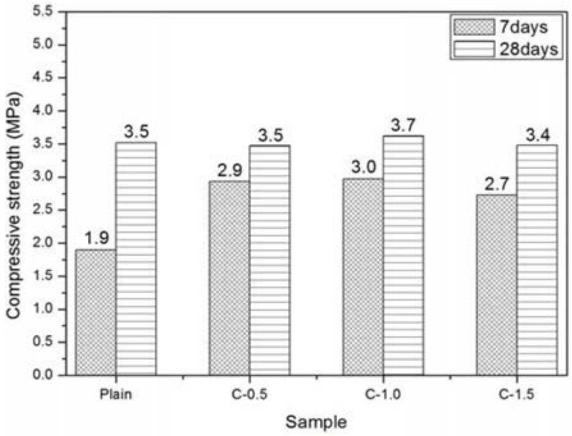

Fig. 4. Compressive strength of mortar containing corn starch with mixing ratio.

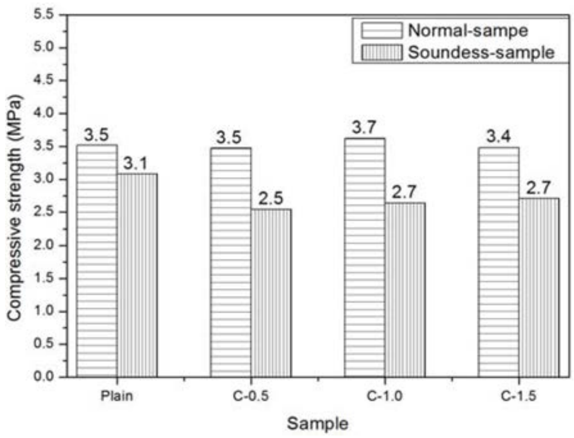

Fig. 5. Compressive strength of mortar containing corn starch after soundness test.

standards requires the evaluation of physical properties such as air content, soundness, and setting time except for compressive strength. Table 4 shows the evaluation results of the physical properties of the NHL mixed with organic admixtures. The air content, soundness, and setting time all satisfied the EU standards. The initial setting time and the final setting time were shortened by the addition of the organic admixtures with a maximum of 14 hrs 30 minutes and 16 hrs, respectively. This indicates that the organic admixtures have an excellent effect on the setting. The NHL Grades according to the EU standards are classified with reference to the compressive strength and setting time on 28 days. The final setting time should be less than 40 hrs for NHL 2, less than 30 hrs for NHL 3.5, and less than 15 hrs for NHL 5 [6]. As shown in Table 4, the setting time property corresponding to NHL 5 may be expressed in the NHL 3.5 sample (plain sample) by adding an organic admixture.

The physical properties of NHL depending on the kind of organic admixtures were evaluated, and the result showed that the NHL mixed with corn starch showed the best physical property enhancing effect and applicability. The optimal mixing ratio was derived by evaluating the physical properties depending on the mixing ratio.

Fig. 4 shows the measured compressive strength of the NHL mortar depending on the corn starch mixing ratio. The measurement result showed that the compressive strength on 7 days and 28 days increased as the corn starch mixing ratio increased. The compressive strength at a mixing ratio of 1.5% was lower than that at 1.0%, indicating that the appropriate corn starch mixing ratio may be less than 1.0%.

Fig. 5 shows the compressive strength measured after performing a soundness test with the NHL mortar mixed with corn starch. The measurement was performed to investigate thermal stability. The compressive strength measurement showed that the compressive strength decreased after a soundness test was performed in all the samples. The decrease in the compressive strength was more distinctive in the sample mixed with corn starch. The heating of starch suspension can cause an interaction between starch particles and water molecules, wherein starch molecules are indirectly bound with each other through the hydrogen bonds of water molecules [14]. The starch continuously swells by the heating and the bonding between starch molecules becomes weak. This process is called starch gelatinization. Generally, starch gelatinization occurs at 60 to 80 °C. During the soundness test where the starch was exposed to steam at a temperature of 90 °C or higher, the conditions for starch gelatinization may have been satisfied. As a result, the compressive strength might have decreased as the corn starch gel, which served as a binder between hydraulic mineral phases and aggregates, was degraded [8, 14].

Table 5 shows the evaluation results of the physical properties of the NHL mortar depending on the corn starch mixing ratio. The air content was less than 5%,

Table 5. Physical properties of hydraulic lime containing corn starch with mixing ratio.

Sample	Air content (%)	Soundness (mm)	Setting time	
			Initial	final
Plain	2.2	−0.2	18 h	23 h
C-0.5	2.7	–	7 h 30 min	10 h
C-1.0	2.6	−1.0	5 h 30 min	7 h 30 min
C-1.5	3.4	−1.3	5 h	7 h

which satisfied the EU standards, regardless of the mixing ratios. With regard to the soundness, slight shrinkage was found as the mixing ratio increased. The shrinkage may be because of the starch gelatinization during the soundness test, which may have destroyed the pore structures inside the hardened body formed by the starch gel. However, the soundness may not be significantly affected because the shrinkage was less than ± 2 mm. The setting time decreased as the corn starch mixing ratio increased. The decrease in the setting time may be because the bonding between the particles inside the hardened body was increased by the starch gelation.

As described above, considering the overall physical properties of NHL mixed with organic admixtures, corn starch may be the most appropriate among the four organic admixtures to compensate the physical properties. In addition, the optimal mixing ratio of corn starch may be about 1%.

Conclusions

The applicability of organic admixtures was investigated to extend the scope of NHL applications, and the following conclusions were made in the present study:

(1) When four organic admixtures of potato starch, corn starch, cellulose, and gelatin were mixed, the NHL flow slightly decreased in comparison with the plain sample. The best flow was found in the sample mixed with corn starch among the four organic admixtures.

(2) The initial strength increased after the addition of the organic admixtures. The compressive strength measured on 7 days was 2 MPa, which is a value that corresponds to the NHL 5 of the NHL classification according to the EU standards.

(3) The compressive strength depending on the corn starch mixing ratio was measured, and the result showed that the strength was not greatly varied by the mixing ratio. However, the compressive strength decreased as the mixing ratio increased to a value higher than 1.0%, indicating that the appropriate corn starch mixing ratio may be less than 1.0%.

(4) The compressive strength measurement showed that the compressive strength decreased after a soundness test was performed in all the samples. The decrease occurred more in the sample mixed with corn starch than in the plain sample because of the starch gelatinization. However, a decrease in the strength did not show a tendency depending on the corn starch mixing ratio.

(5) The setting time depending on the corn starch mixing ratio was measured, and the result showed that the setting time increased as the mixing ratio increased. However, considering the compressive strength and other physical properties, the appropriate mixing ratio may be 1.0%.

(6) The physical properties depending on the kind of organic admixtures and the corn starch mixing ratio were evaluated, and the result showed that all the tested physical properties satisfied the EU standards. Therefore, the organic admixtures may be applied to improve the performance of NHL depending on the fields of application.

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