

Dependence of alkali activator coating on aggregates upon mechanical strength of geopolymer/aggregates composites

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In this study, geopolymers were reinforced with artificial aggregates, and the effect of the coating of the aggregates with various solutions on the strength of the composites was analyzed. The applied alkaline coating solutions were sodium silicate and NaOH. The composites made with coated aggregates had a higher compressive strength than specimens made with pure aggregates, regardless of kinds of coating solutions. That was possible because the geopolymers paste kept their fluidity during the forming process; thus, the coating layer of the aggregates prevented the aggregates from absorbing water. In addition, a high concentration of NaOH in the vicinity of the boundary between the matrix and the aggregates enhanced the geopolymeric reaction, which in turn increased the compressive strength of the composites. In particular, when the geopolymer was combined with aggregates coated with NaOH of 16 M, the resulting composite had a compressive strength of 32.2 MPa, which is about six times higher than that of composites with pure aggregates. With the advantage of light weight, the composites fabricated in this study can be used in various fields, such as insulation boards, sound proofing materials, fire protecting materials, and chemically resistant materials.

Key words: Aggregate, Coating, Geopolymer, Coal Ash.

Introduction

Ordinary cement has commonly been used as a glue in civil engineering and construction projects. However, cement production consumes a large amount of energy and generates a huge amount of CO₂ gas when the main raw materials of cement are burned, particularly limestone (CaCO₃) [1]. The amount of cement manufactured increases by 3% annually, and the amount of CO₂ gas discharged from the cement production process is about 1.3 million tons per year, which accounts for 7% of global greenhouse gas emissions. Recently, geopolymers have attracted attention as substitutes for cement because they generate close to zero CO₂ in the manufacturing process. Geopolymers can be hardened by mixing minerals composed of silica and alumina with a glassy state and an alkaline activator using a poly-condensation process without a firing process [2].

A geopolymer has a non-crystalline three-dimensional network structure composed of aluminosilicate and has excellent mechanical properties, chemical durability and fire resistance while also having the advantage of being producible from industrial waste or low-grade materials [3–7]. When aluminosilicate material with a glassy state is put in an alkaline environment, Si and Al ions elute and a polymerization process rapidly proceeds at the

same time to form a geopolymer with a three-dimensional polymeric chain structure, such as -Si-O-Al-O bonds [8–10].

Recently many studies have focused on developing secondary products from geopolymers. For example, composites of geopolymers and artificial aggregates with various properties can be used in various fields such as sound absorption materials, lightweight materials, materials for agriculture, and materials for purifying contaminated soil or water.

In this study, we reinforced geopolymers with artificial aggregates and investigated the effect of coating the aggregates with various solutions on the strength of the composites. For these purposes, three types of coating solution, water, sodium silicate and NaOH, were applied to find optimizing conditions for creating geopolymer/aggregate composites with a high level of strength. We also analyzed the mechanical properties of the fabricated geopolymers/aggregate composites from the view point of microstructure and various parameters for the coating process

Experimental Procedures

Coal reclamation ash for raw materials

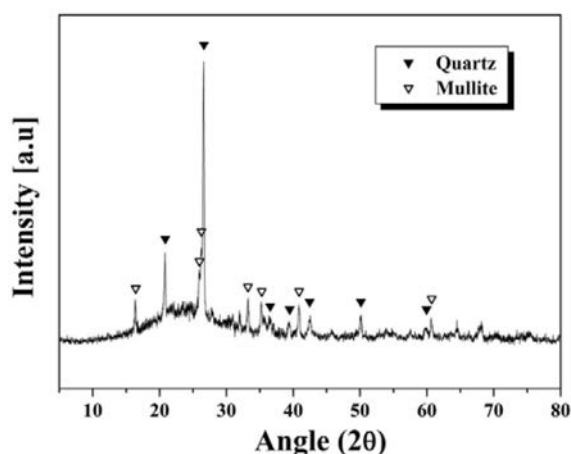
The source material for the geopolymer was coal reclamation ash (denoted as CRA) discharged from the ‘S’ thermal power plant in South Korea. The chemical composition of the CRA was determined by X-ray fluorescence (XRF, ZSX Primus, Rigaku, Japan) and is shown in Table 1.

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Table 1. Chemical composition of the coal reclamation ash (wt%).

SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	Fe ₂ O ₃	MgO	K ₂ O	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	C	I.L.*	Total
52.4	19.2	0.5	3.5	10.8	1.1	1.3	1.0	0.3	0.2	7.5	3.6	100

*I.L.: Ignition loss.

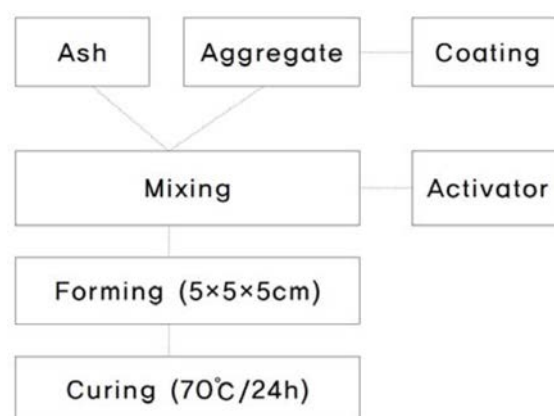
**Fig. 1.** XRD patterns of the starting materials of the coal reclamation ash used in this study.

The amounts of SiO₂ and Al₂O₃ were 52.4 and 19.2 wt%, respectively, which were sufficient for use as a starting material for the geopolymer material. The ash contained a small amount of CaO of less than 10 wt%, so it was classified as F-class ash. The phase analysis performed by X-ray diffractometer (XRD, Rigaku MiniFlex2) for the starting materials is shown in Fig. 1. The main crystal phases were quartz (SiO₂) and mullite. The coal reclamation ash was dried at 105 °C for 24 h and crushed using a pin mill to less than 53 μm before use.

Fabrication of artificial aggregates

The artificial aggregates were fabricated using red clay, stone sludge and spent bleaching clay. They were mixed with a ratio of red clay : stone sludge : spent bleaching clay = 6 : 3 : 1 by weight. The raw materials were dried at 105 °C for 24 hrs and crushed using a pin mill to less than 100 μm before use. The mixture was formed into sphere shape of 1-5 mm diameter using a granulator.

The formed granules were then dried at 110 °C for 48 hrs using a hot-air drying machine and fired in a

**Fig. 2.** The procedure for fabricating the geopolymer/aggregate composites.

rotary kiln at 1125 °C/15 min. The density, absorption rate and unit volume weight were 1.7 g/cm³, 12%, and 1.04 ton/m³ respectively.

Coating on the aggregates

The aggregates were dried for 100 °C/24 hrs before the coating process was begun. Then the aggregates were coated with three kinds of solution by the dipping method for 24 hrs followed by drying at 100 °C/24 hrs. Three types of coating solution, deionized water, sodium silicate and NaOH, were used. The aggregate coated with water was mixed with the geopolymers right away after coating without a drying process while the specimens coated with alkaline solution were dried. The sodium silicate solution was prepared by mixing sodium silicate (first grade, SiO₂=35-38, Na₂O=17-19 wt%, Kanto Chemical Co. Japan) with water 0-80 wt%. The molarity of the NaOH solution used was 4-24 M.

Fabrication of the geopolymer/aggregate composites

The procedure for geopolymer/aggregate composites is shown in Fig. 2. The experimental parameters used to fabricate the geopolymer/aggregate composites are

Table 2. Processing parameters for fabricating the geopolymer/aggregates composites.

Coating solution	Raw materials	Amount of aggregate	Activator concentration	L/S ratio	Coating solution concentration
NaOH	CRA*	70 wt%	16 M	0.5-0.8	4-24 M
Water				0.7	—
Sodium silicate				—	—

*CRA: coal reclamation ash.

shown in Table 2.

The raw material, aggregates coated and alkali activator solution were mixed and then rapidly poured into a brass cubic mold ($5 \times 5 \times 5$ cm) and sealed from the atmosphere. The green specimen, cured at 70°C for 24 hrs, was covered with a polyethylene zipper bag to prevent the evaporation of moisture and to maintain an internal humidity of 99%. The amount of aggregates added was 70%.

The compressive strength of the cylindrical geopolymer was measured using an UTM (UTM-900NJ Series Daekyung, Korea) with a head speed of 5 cm/min. The compressive strength value was obtained from the average values of three measured specimens. The microstructure of the geopolymer was observed using a scanning electron microscope (S-4800, Hitachi, Japan) with secondary electrons accelerated by a voltage of 5 kV. The specimens were coated with platinum using an evaporator prior to the SEM imaging step.

Results and Discussion

Amount of aggregates added

The compressive strength of geopolymer/aggregate composites as a function of the amount of aggregates added is shown in Fig. 3. The compressive strength of the pure geopolymers was 15.7 MPa and decreased with the amount of aggregates added.

The decrease in compressive strength with the addition of lightweight aggregates may have been caused by the many pores reside in the aggregates. Generally, the compressive strength of a concrete decreases with the addition of porous aggregates because of the pores in the aggregates [11, 12].

Effect Kinds of Coating Solution

The compressive strength of the geopolymer/aggregate composites as a function of the kind of coating

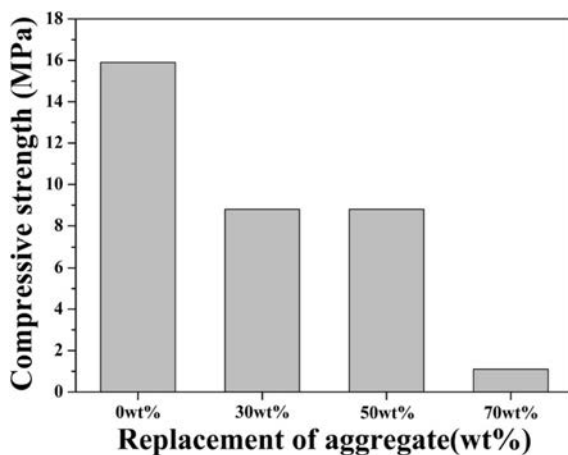


Fig. 3. The compressive strength of the geopolymer/aggregate composites according to the amount of aggregates added. The liquid/solid ratio used was 0.4.

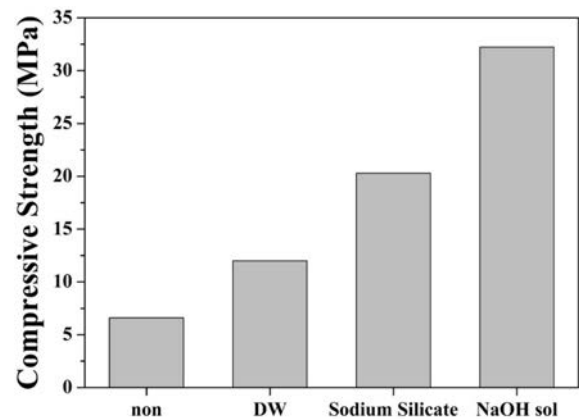


Fig. 4. The compressive strength of geopolymer/aggregate composites as a function of the kinds of coating solution coated on the aggregates. The liquid/solid ratio was 0.7.

solution coated on the aggregates is shown in Fig. 4. The compressive strength of geopolymer/aggregate composites was 6.6 MPa. This relatively high value compared to that in Fig. 3 is due to a higher liquid/solid ratio of 0.7. In addition, the compressive strength of the geopolymer/aggregate composites using coated aggregates was higher than that using non-coated aggregates, regardless of kind of coating solutions. In particular, the compressive strength of the geopolymer/aggregate composites using aggregates coated with NaOH solution was 32.2 MPa, which is six times higher than that using non-coated aggregates.

The composites with coated aggregates had higher compressive strength than the specimens with pure aggregates regardless of kind of coating solution. That was possible because the geopolymer paste could keep its fluidity during the forming process owing to prevent the coating layer aggregates from absorbing water. The fluidity of mortar is one of the essential factors that contribute to the mechanical strength of concrete [13-16].

When the aggregates absorb part of water in the forming process, the fluidity and workability of the mortar and the packing efficiency and bonding coherence between the matrix and aggregates decrease. Therefore, aggregates wet by water or coated with alkaline solution can minimize the water absorbing from the matrix during the forming process of geopolymer/aggregate composites. In addition, the high concentration of NaOH in the vicinity of the boundary between the matrix and the aggregates enhanced the geopolymeric reaction, which increased the compressive strength of the composites. The microstructure of the geopolymer/aggregate aged for one day as a function of the type of coating solution on aggregates is shown in Fig. 5. There were no certain differences in the microstructure magnified by 50 times. The microstructure of the specimen using aggregates coated with coating solution, however, had a dense and homogeneous

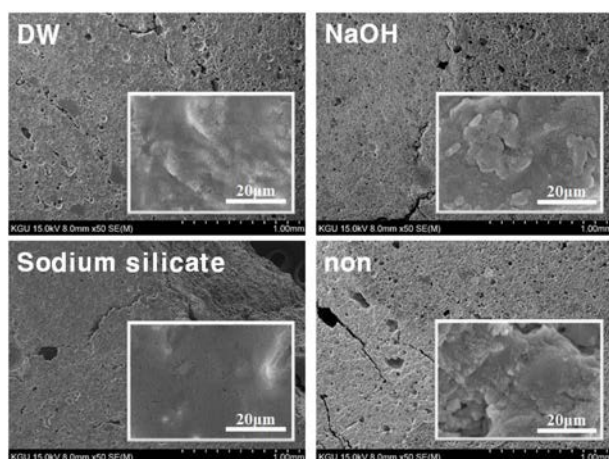


Fig. 5. Microstructure of the geopolymer/aggregate composites according to the type of coating solutions used for coating on aggregates.

morphology. In addition, the composites using aggregates coated with NaOH had small grains, which we determined to be zeolite, which was evidence of geopolymeric reaction.

Considering the results of Figs. 4 and 5 together, the strength of the composites using pure aggregates was lower than expected because the aggregates absorbed the water from the matrix, which decreased the fluidity and workability of the mortar and lowered the dense packing of the mortar during forming process. Meanwhile, the composites with aggregates wet with water did not lose fluidity during the forming process and had a relatively homogeneous microstructure, which improved the mechanical strength.

In the composites with aggregates coated with alkaline solution, there were both effects of pore saturation and acceleration of the geopolymeric reaction. The polymeric reaction was accelerated due to diffusing of the alkaline components to the surrounding matrix. Further, among the alkaline solutions, the NaOH was more effective than sodium silicate.

Liquid/solid ratio

The compressive strength of geopolymer/aggregate composites as a function of the liquid/solid ratio is shown in Fig. 6. The molarity of the NaOH solution was 16 M. The compressive strength of the geopolymer/aggregate composites increased with the liquid/solid ratio showing the maximum value at a liquid/solid ratio of 0.7. When the liquid/solid ratio is below 0.7, the fluidity seems to be insufficient to offer better packing of all constituents in mortar during forming process.

When the liquid/solid ratio, however, is higher than 0.7, the evaporation of excessive water creates pores in the microstructure so the optimum liquid/solid ratio is determined as 0.7. The microstructure at the vicinity of the boundary between the matrix and aggregates of the composites according to variation of the liquid/solid

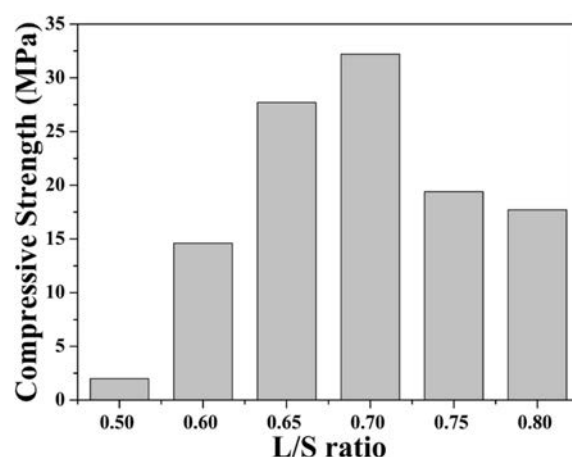
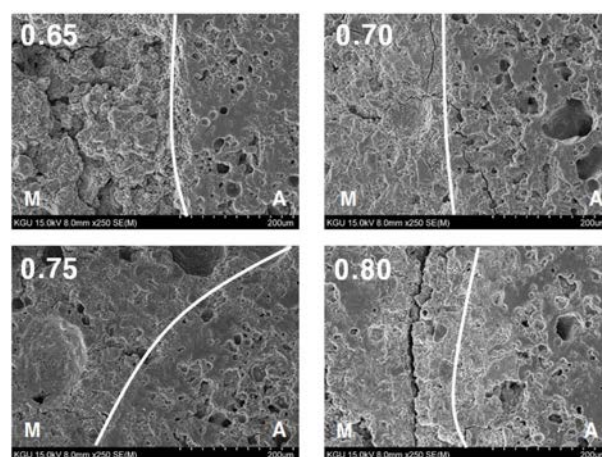


Fig. 6. The compressive strength of the geopolymer/aggregate composites as a function of the liquid/solid ratio. The molarity of NaOH solution was 16 M.



M : mortar, A : aggregate

Fig. 7. The microstructure in the vicinity of the boundary between the matrix and aggregates of the composites according to a variation of the liquid/solid ratio. The parts marked M and A represent matrix and aggregate, respectively.

ratio are shown in Fig. 7. The parts marked M and A represent the matrix and aggregate, respectively. The aggregates are more porous than the matrix.

The matrix of composite made with a liquid/solid ratio of 0.65 did not have a dense microstructure in which cracks, voids and pores existed, while the matrix with a liquid/solid ratio of 0.7 had a very dense microstructure. When considering this observation combined with the compressive strength in Fig. 6, the strength of the composites increases when the microstructure in the vicinity of the boundary between the matrix and aggregates become denser.

Concentration of sodium silicate solution

The compressive strength of geopolymer/aggregate composites as a function of the concentration of a sodium silicate solution is shown in Fig. 8. The compressive strength of the composites increased with

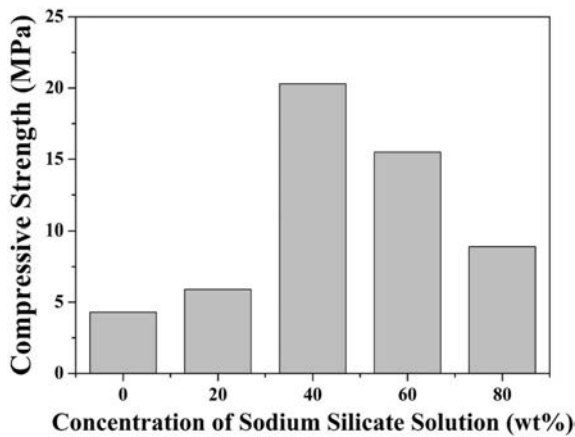


Fig. 8. The compressive strength of composites using aggregates coated with sodium silicate as a function of the concentration of the sodium silicate solution. The liquid/solid ratio used was 0.7.

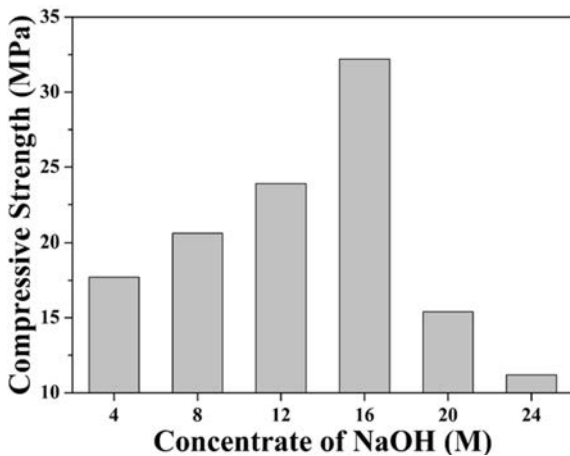


Fig. 9. The compressive strength of composites using aggregates coated with NaOH as a function of molarity of NaOH. The liquid/solid ratio was 0.7.

an increasing concentration of sodium silicate solution and was maximum at a concentration of 40 wt%.

The hydrolysis reaction for sodium silicate occurs as Eq. (1):



Thus, the alkalinity should increase with sodium silicate in the water. The geopolymeric reaction, therefore, will be enhanced in the vicinity of the boundary between the matrix and the aggregates when the geopolymers are reinforced with aggregates coated by sodium silicate. The excessive alkalinity, however, seems to obstruct the poly-condensation reaction of geopolymers because the compressive strength of the composites decreased when the concentration of sodium silicate in the water was above 40%.

Molarity of NaOH solution

The compressive strength of composites using aggregates coated with NaOH as a function of the

molarity of NaOH is shown in Fig. 9. The liquid/solid ratio was 0.7. The compressive strength of the composites increased with the molarity of NaOH solution coated on aggregates and showed a maximum at a molarity of 16 M.

As the molarity of NaOH solution increased, the more Si and Al ions can be dissolved out of a matrix of coal ash, which accelerated the geopolymeric reaction and improved the compressive strength of specimens [17-19]. Increased compressive strength with alkalinity was very similar to the trend for composites using aggregates coated with sodium silicate. The geopolymeric reaction occurred actively near the boundary between the matrix and the aggregates when the aggregates were coated with NaOH. A too high molarity of NaOH, however, controls the poly-condensation reaction of geopolymers [20].

Conclusions

In this study, we fabricated geopolymer/artificial aggregate composites and analyzed the effect of coated aggregates with various conditions on strength of the composites. The compressive strength of the geopolymer/aggregate composites with coated aggregates was higher than that of non-coated aggregates, regardless of the kind of coating solutions because of the more homogeneous microstructure obtained. That was possible because the geopolymer paste kept its fluidity during the forming process because the coating layer prevented the aggregates from absorbing water. Among the three coating solutions applied, the NaOH was proven as the optimum one for improving the compressive strength of the composites. In particular, when the geopolymers were combined with aggregates coated with NaOH of 16 M, the resulting composite had a compressive strength of 32.2 MPa, which was about six times higher than that of the composites using pure aggregates. The reason the composites with aggregates coated with alkaline solution had much higher strength is that a geopolymeric reaction occurred actively near the boundary between the matrix and the aggregates. The microstructure of the specimens using aggregates coated with NaOH had small grains, which we determined to be zeolite, which was evidence of a geopolymeric reaction. An excessively high concentration of NaOH, however, controlled the poly-condensation reaction of the geopolymers, resulting in a decrease in compressive strength of the composites.

Acknowledgments

This work was supported by Kyonggi University Research Grant 2014.

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