O U R N A L O F

Ceramic Processing Research

Study on properties of geopolymer-polyurethane sponge composite

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A newly conceived geopolymer composite was fabricated by a combination of the geopolymer and polyurethane sponge. The density and porosity of hardened geopolymer composite, corresponded to different pore sizes of polyurethane sponge, exhibited no significant differences from each other. However, the mechanical behavior, the compressive strength and flexural strength, showed slight differences accordingly. Fracture of the geopolymer composite exposed to high compressive load was not observed from all specimens containing polyurethane sponge. The toughness enhancement of the geopolymer composite, due to spontaneous elasticity of polyurethane sponge, crack spread, and crack diffraction, was identified through the stress-strain curve and microstructure of fracture surface. The newly designed geopolymer composite having a 3-dimensional sponge skeleton showed relatively higher flexural strength of 8.0 MPa than other conventional geopolymer composites.

Key words: Geopolymer, Polyurithane, Composite, Compressive strength, Flexural strength.

Introduction

Geopolymer consists of silica (SiO₂) and alumina (Al_2O_3) ; it is the inorganic composite hardened through the reaction of strong alkali-basic solution. In the latter half of the 1970s, Davidovits, the French polymer chemist, developed a material of the structure similar to zeolite by an activation of alumina silicate with basic solution [1-5]. The newly invented material was named as geopolymer due to its 3-dimensional structure similar to polymers resulted from the polymerization of alumina silicate. The geopolymer is a kind of alkaline alumino-silicate cement and it has advantages of low level of CO₂ emission, high thermal resistance, chemical resistance, and excellent mechanical properties comparing to those of Portland cement [6-9]. Along with recent environmental concerns resulted from global warming that have been regarded as social issues, the studies, delving into the development of new geopolymers of improved physical properties, are in progress continuously heading for the commercialization of environmentally friendly hardened body of geopolymers of no CO₂ emission instead of producing conventional cement [9-11].

Currently, the studies intending for the development of monolith, as well as composites, of geopolymers integrated with other materials, are in progress. Geopolymer composites which are designed to have properties superior to those of simple geopolymers by the integration with alumina aggregate, cotton fibers, bamboo fibers, or pine trees, are currently employed in several industries as new materials for future construction purposes etc. Such geopolymer composites typically exhibit compressive- and flexural strength distributing in respective ranges of 45~90 MPa and 3.0~7.5 MPa; the difference in physical properties thereof depends on the designed composition of each material [12-15].

In the present study, the changes in physical properties and behaviors associated with porosity of geopolymer were examined by applying alkaline stimulants as well as sodium silicate solution to the basic solution to control the microstructure of geopolymer. Under the given conditions, the polyurethane sponge having 3-dimensional network structure was employed as a polymer to control mechanical properties of the designed geopolymer-polyurethane composite. The size of pores in the polyurethane sponge was varied to examine resulting mechanical properties of the geopolymerpolyurethane composite to be varying accordingly.

Experimental Procedure

Fabrication process of the geopolymer-polyurethane sponge composite is illustrated in Fig. 1. As a starting material for fabrication of the geopolymer, the metakaolin was used. Composition of meta-kaolin is presented in Table 1. Ratio of meta-kaolin powder to mixing solution (the solution of alkaline stimulant (40 wt% potassium hydroxide solution) mixed with water glass (sodium silicate solution)) was fixed by 1:1 wt%, whereas the mixing ratio of alkaline stimulant to water glass was fixed by 1:2 wt%. Water glass was added to the aqueous solution of alkaline stimulant and then the solution was agitated for 10 minutes to make

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Fig. 1. Fabrication process for geopolymer-polyurethane composite.



Fig. 2. Image of polyurethane sponge.

completely mixed solution; the mixed solution was then added to the meta-kaolin powder to produce the geopolymer slurry. The produced slurry was then kneaded for 10 minutes at low speed and for 10 minutes at high speed with the use of magnetic stirrer; the stirred slurry of geopolymer was then poured into the rounded plastic mold of 15×60 mm filled with the polyurethane sponge from which the specimens were derived after 5 minutes while the sponge was soaked up in the slurry. Representative forms of polyurethane sponges used for the experiment conducted in the present study are presented in Fig. 2. Pore size of sponge (pore per inch (PPI)) was varied in the range 10 ~ 60 PPI for the experiment. The prepared specimens were put into the dryer and cured at 60 °C therein for 24 hours thereby the solid phase specimens of hardened geopolymer-polyurethane composite were fabricated. The produced specimens of hardened geopolymerpolyurethane composites were detached from the mold and then the physical properties thereof such as porosity, density, compressive strength, flexural strength, and

Table 1. Chemical compositions of kaolin.

Component	wt%
SiO ₂	53.0
Al_2O_3	44.0
Fe ₂ O ₃	0.25
MgO	0.22
CaO	0.4
K ₂ O+Na ₂ O	0.23

microstructures etc. were examined.

Archimedes method was used to analyze porosity and density of the fabricated hardened geopolymerpolyurethane composite for which the kerosene was employed as a solvent to prevent the residual alkaline solution from being diluted in water after the reaction with specimen. To measure the compressive strength of specimens, the universal testing machine (UTM 5589, INSTRON, U.K) was used for which the specimens of cylindrical form were prepared. At the level of loading of 600 KN, the test was carried out with the loading speed of 1 mm/min. Flexural strength of the hardened geopolymer-polyurethane composite was measured with the specimens prepared in the shape of bar (6×8) \times 90 mm) for the Fatigue Testing Machine (Model : E1000, INSTRON, U.K); the loading of 1 KN was applied with the cross head speed of 1 mm/min. Scanning electron microscope (FE-SEM, JSM-7100F, Hitachi, Japan) was used for the observation of microstructure of the hardened geopolymer-polyurethane composite. Surface of the composite was observed through an optical microscope (CN/S 100, LeeTech, Korea).

Results and Discussion

Density of the monolithic geopolymer tended to be increasing in accordance with increasing amount of alkaline stimulant added; the mechanical properties thereof also improved accordingly. Microstructures of the starting powder of meta-kaolin and hardened geopolymer are presented in Fig. 3. Particle sizes did not render significant differences after hardening; as a whole, the porous structures thereof were found. Such structure of porous body is frequently found from geopolymers; the hardened body of approximately 29.6% of porosity was obtained from the experiment wherein the ratio of alkaline stimulant to glass water was fixed by approximately 1:2 wt%.

Porosity and density of geopolymer-polyurethane composite

The porosity and density of the geopolymer composite are presented in Fig. 4. The porosity tended to be increasing slightly with an addition of the sponge of 3-dimensional network structure to geopolymer, whereas the density thereof tended to be decreasing accordingly. Porosity of all specimens showed around Study on properties of geopolymer-polyurethane sponge composite



Fig. 3. SEM morphologies of (a) metakaoline and (b) monolithic geopolymer fabricated by 1:2 ratio of potassium hydroxide solution to sodium silicate solution.



Fig. 4. Porosity and density of geopolymer-polyurethane composites at each different PPI.

30%, and the density was in the range $1.46 \sim 1.48 \text{ g/cm}^3$. The porosity and density, which were almost remaining unchanged despite an addition of polyurethane sponge to geopolymer, suggest that the density of polyurethane sponge is almost similar to the density of geopolymer. Fig. 5 shows microstructures of the geopolymer composite at each PPI. For all specimens, the pores therein were filled densely with the hardened geopolymer. Sponge skeleton of wide area is observed from the polyurethane sponge of small PPI wherein the



Fig. 5. Polished surface of geopolymer-polyurethane composites at each PPI.



Fig. 6. Compressive strength of geopolymer-polyurethane composites at each sample having various PPI.

differences in density thereof are insignificant; this suggests the density of dense skeleton of sponge is similar to the density of the monolith of porous geopolymer.

Compressive strength of geopolymer-polyurethane composite

Fig. 6 illustrates the deformation of geopolymerpolyurethane composite resulted from an application of compressive load. The monolith geopolymer, free from the polyurethane sponge, had a fracture at the loading of approximately 270 KN (121.5 MPa). However, the specimens, containing the sponges, exhibited continuous deformation without fracture despite continuous increase of compressive loading. Point of inflection at the level of loading around 270 KN was observed except for the specimen of 60 PPI. The reason behind the appearance of inflection point is estimated to be attributable to the crack spreading phenomenon of microcracks which were created by compressive loading applied to the porous geopolymer matrix; but the progress thereof was disturbed by 3-dimensionally distributed polyurethane sponge. Thus, the point, where the slope of curve becomes



Fig. 7. Morphologies of geopolymer-polyurethane samples after compressive strength test.

reduced for all specimens containing polyurethane sponge, seems to be the point of cracks in the matrix of geopolymer to be spread by the polyurethane sponge of 3-dimensional network structure. We can see the compressive deformation continues by elastic properties of polyurethane sponge exposed to continuing compressive loading. For the case of 60 PPI specimen, the part of inflection was observed distinctly with low slope of curve; this was estimated to be attributable to microcracks passing through the sponge due to relatively thin skeleton of the sponge, and to the relatively larger strain of the specimen entirely kept by 3-dimensional network covering of the sponge of relatively low Young's modulus.

Fig. 7 shows the shapes of specimens completed the test. The monolithic geopolymer was broken under the compressive load, whereas the specimen containing 60 PPI polyurethane sponge remains without fracture despite the high compressive loading. These results were estimated to be attributable to the suppression of the development of microcracks toward bigger cracks by the trapping microcracks inside of pores of the polyurethane sponge, and to the absorption of compressive stress by the elastic strain of sponge. According to previous studies [12, 13], the compressive strength of geopolymer containing alumina aggregate was 90 MPa. Besides, the geopolymer, containing cotton fiber, exhibited its compressive strength lower than this level. Comparing to the composites, to which the fillers lacking continuity were added, the geopolymer, to which the 3-dimensional polyurethane sponge was added, manifested distinct increase in compressive strength.

Flexural strength of geopolymer-polyurethane composite

The results of flexural strength test of the geopolymer composite are presented in Fig. 8. The interval of crack energy absorption, different from an ordinary brittle failure behavior, was observed from the geopolymer composite containing polyurethane sponge, whereas the flexural strength was found increasing in accordance with increasing values of PPI. For the specimen of 60 PPI, the maximum strength was 8.0 MPa. Stress-strain curve of the geopolymer composite containing the reinforcement of bamboo fiber showed



Fig. 8. Stress-strain curves of geopolymer-polyurethane composites for flexural strength test at each sample having various PPI.



Fig. 9. Fracture surface of geopolymer-polyurethane composites after bending test.

crack diffraction by the reinforcement and resulted in ductile behavior owing to an absorption of stress; it's measurement of maximum flexural strength was 7.5 MPa [14]. In the fracture surface of specimens containing bamboo fibers, the "pull-outs" of part of bamboo fibers were observed that suggested the absorption of crack energy. The specimen of geopolymer containing polyurethane sponge showed unique fracture behavior; approximately 0.15 mm of strain together with the absorption of stress under given strength were observed. This was estimated to be attributable to the microcracks spread and propagation along the 3dimensional skeleton of polyurethane sponge. Thereby, the cracks propagated over entire specimen just like spider web. The strain of specimen also occurred by the elasticity of sponge. Finally, the fracture of specimen happened at higher load with sudden progress of the microcracks.

Fig. 9 shows the microstructures of fracture surface resulted from the test of flexural strength. For the case of monolithic geopolymer, the fracture surface, which is available from the brittle fracture of ordinary ceramic materials, is presented, whereas the fracture surface of the specimen containing the polyurethane sponge of 60 PPI shows the geopolymer, that filled pores of sponge and some of them were protruded just like the "pullouts" of fibers. The phenomenon suggests the cracks are diffracted to every direction along the skeleton of Study on properties of geopolymer-polyurethane sponge composite







Fig. 11. Optical microscope image of geopolymer-polyurethane interface.

polyurethane sponge. Thus, such phenomena appear more according to increasing PPI of polyurethane sponge; the measurements of strength also tended to be increasing in accordance with increasing value of PPI.

Crack diffraction occurred in the geopolymerpolyurethane composite is presented in Fig. 10. Diffraction of crack was observed from the skeleton of sponge. The diffraction was estimated to be resulted from a mechanism different from that of the crack diffraction on the weak interface between ceramic matrix and fibers appearing from ordinary fiberreinforced ceramic composites. Fig. 11 is a zoomed-in image of an interface between geopolymer and sponge wherein the dense structure of interface is shown. Based on these results, the weak structure of sponge seems providing the cracks with pathways of diffraction.

Conclusions

In the present study, the matrix of geopolymer, prepared with the use of meta-kaolin, and the polyurethane sponge, were integrated together to produce the ceramic-polymer composite. The properties of the geopolymer - polyurethane sponge composite are as summarized in the following:

1) The integration of geopolymer with polyurethane sponge rendered no significant effect over porosity and density thereof, however the fracture resistance against compressive loading and toughness were found improved; the mechanical properties varied according to PPI of the sponge.

2) Flexural strength of geopolymer-polyurethane composite appeared increasing in accordance with increasing level of PPI with some "pull-outs" observed. Propagation of microcracks in the specimen tended to be suppressed by 3-dimensional network structure of sponge.

3) Diffraction of cracks appeared by the spontaneous weak structure of polyurethane sponge; the phenomenon was influenced by PPI of sponge to a certain extent.

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