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Synthesis of Geopolymers from Mechanically Activated Coal Fly Ash and Improvement of Their Mechanical Properties

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Abstract: Coal fly ash is a spherical fine powder by-product discharged from coal-fired power plants. When coal fly ash is used as raw materials for the synthesis of geopolymers, there are practical problems associated with the stable surface of the particles that do not allow the production of geopolymers with sufficient strength. A long-time is also required for the curing. In this study, we aim to promote the curing reaction of geopolymers by activating the surface of coal fly ash particles. By mechanically activating the surface of coal fly ash particles using an attrition-type mill, the dissolution of Si^{4+} and Al^{3+} in coal fly ash is promoted, and the acceleration of the reaction taking place during curing is also anticipated. The surface morphology and crystal phase of coal fly ash particles change with the use of an attrition-type mill. The mechanical activation results in improvement of the compressive strength and the acid resistance under milder curing conditions by the densification of the hardened body. Thus, it is clearly shown that mechanical activation is effective for the production of geopolymers with beneficial mechanical properties under milder curing conditions.

Keywords: coal fly ash; mechanical activation; geopolymerization; compressive strength

1. Introduction

Geopolymers are an amorphous polymer obtained by condensation polymerization with dehydration when the Si^{4+} and Al^{3+} from the aluminosilicate powder are dissolved with an alkali solution [1–5]. Geopolymers have tetrahedral frameworks of SiO_2 and AlO_4 like that of zeolite structure [6,7]. Unlike cement, which requires a firing process using a large amount of energy, geopolymers are expected as a low CO_2 emission structural material. From the viewpoint of effective utilization of coal fly ash, geopolymers have been drawing attention in recent years. Coal fly ash is a spherical fine powder by-product discharged from coal-fired power plants and is mainly composed of SiO_2 and Al_2O_3. There are two types of coal fly ash, such as class F and class C. The class F fly ash contains less than 7% of CaO, and the class C fly ash contains more than 20% of CaO. When coal fly ash is used as raw materials of geopolymers, there are practical problems, such as the surface of coal fly ash particles are stable, and thus the strength of geopolymers is difficult to develop at room temperature [8]. A long-time is also required for the curing of geopolymers [9]. It has been reported

that the dissolution of fly ash is not complete before the final hardened body is formed [10]. It is known that applying mechanical energy by a mechanical treatment improves the reactivity of bulk and surface of materials [11–13]. When the surface of coal fly ash particles is activated by mechanical treatment, the curing reaction of geopolymers can be accelerated [14–19]. When the curing reaction of geopolymers is accelerated, the dissolution of Si^{4+} and Al^{3+} in coal fly ash is promoted, and the mechanical properties of geopolymers are developed even under mild curing conditions. It has been reported that the effect of particle size and specific surface area on the increase of the dissolution of Si^{4+} and Al^{3+} in coal fly ash [20]. Also, many mechanical activation methods may affect the size reduction of coal fly ash particles. It has been reported that the reduction of particle size improved the rate of geopolymerization reactions [21,22]. It has also been reported that the strength of the geopolymer was improved by applying the high activity of the nanoparticles [23,24]. It is still unclear what the effect of the surface activation of coal fly ash particles by the mechanical treatment has on the acceleration of the curing reaction and mechanical properties of geopolymers.

In this study, we aimed to promote the curing reaction of geopolymers by activating the surface of coal fly ash particles, which were raw materials of geopolymers. The surface of coal fly ash particles is activated by the mechanical method using an attrition-type mill. The attrition-type mill is capable of repeatedly applying strong shear and compressive forces to the powder layer between a high speed-rotating rotor and an inner wall of a vessel, activating the surface of particles, and improving the reactivity [25]. The mechanical method using the attrition-type mill changes the surface morphology of coal fly ash particles without grinding media. The amorphization of the surface of coal fly ash particles occurred without the size reduction of particles. The effects of the mechanical activation of coal fly ash particles on the curing reaction and mechanical properties of geopolymers were discussed.

2. Materials and Methods

2.1. Mechanical Activation and Characterization of Coal Fly Ash Powder

The flow chart of the experimental methods of this study is shown in Figure 1. Coal fly ash, having the quality of JIS (Japanese Industrial Standards), was used as a raw material. The coal fly ash powder was mechanically treated using the attrition-type mill for mechanical activation. The inner diameter and height of the used chamber were 80 mm and 50 mm, respectively. The gap between the rotor and the chamber was fixed at 1 mm. The rotation speed of the rotor was increased up to 4000 rpm. The electric power, which was defined as the load power applied to a rotor shaft, was maintained at 1.0 kW for 10, 20, and 30 min. Untreated coal fly ash was named as raw coal fly ash here.

The chemical composition was analyzed by using a silicon drift X-ray detector (X-MAX, Horiba, Kyoto, Japan). Mineralogical characterization of the obtained powder was identified by a powder X-ray diffraction (XRD, RINT-TTR, Rigaku, Tokyo, Japan) using Cu Kα-radiation at 30 kV and 10 mA. The morphology of the obtained powder was examined using an SEM (FE-SEM, Hitachi S-4800, Hitachi High-Technologies, Tokyo, Japan) at 1.0 kV. The particle size distribution was determined using a laser scattering particle size distribution analyzer (LA-950, Horiba, Kyoto, Japan). Small amounts of the samples were dispersed in 0.05 mass% sodium hexametaphosphate solution using an ultrasonic homogenizer.

To evaluate the activation of the surface of coal fly ash particles by the mechanical treatment, the dissolution amount of Si^{4+} and Al^{3+} in an alkaline solution was measured. The raw or mechanically activated (MA) coal fly ashes were dissolved separately in 10 mol/L NaOH, and then the mixed solution was shaken for 3 h using a vertical shaker (SR-2DW, Taitec, Saitama, Japan). After solid–liquid separation, Si^{4+} and Al^{3+} concentration in the filtrate was measured using an inductively coupled plasma atomic emission spectrometer (ICPE-9820, Shimadzu Corporation, Kyoto, Japan).

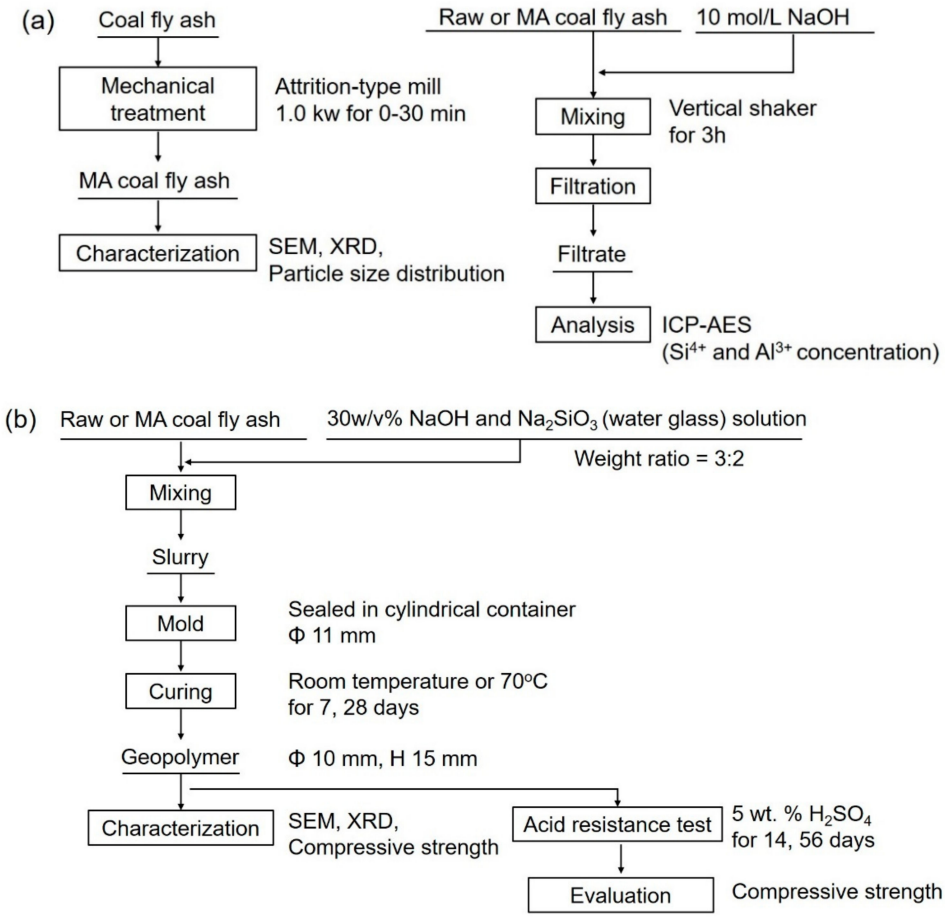

Figure 1. Flow chart of experimental methods for (**a**) mechanical activation of coal fly ash and (**b**) synthesis and evaluation of geopolymers.

2.2. Synthesis and Evaluation of Geopolymers from Mechanically Activated Coal Fly Ash

The raw or MA coal fly ashes were placed separately in a cylindrical container, and a mixed slurry of 30 *w*/*v*% NaOH solution and Na_2SiO_3 as water glass (SiO_2/Na_2O = 2.06–2.31 molar ratio, Wako Pure Chemical Industries, Osaka, Japan) were added to prepare a paste (weight ratio is set to 3:2). The obtained paste was filled and sealed in the cylindrical container, and it was allowed to stand at room temperature (RT) for 24 h to demold the sample. After demolding, it was sealed in the cylindrical container to prevent moisture loss and allowed to stand again at RT or 70 °C for 7 or 28 days to prepare a cured product (10 mm in diameter and 15 mm in height). The obtained geopolymers were evaluated by morphological observation with the SEM, phase identification with the XRD, and compressive strength test with an autograph with a crosshead speed of 0.5 mm/min and a load cell of 5 kN. Three samples were measured for each curing condition to confirm reproducibility. To investigate the effect of the mechanical treatment to coal fly ash on acid resistance of geopolymers, the samples obtained under various curing conditions were immersed in 5 wt. % H_2SO_4 for 14 or 56 days, and the compressive strength tests were carried out.

3. Results and Discussion

3.1. Characterization for Coal Fly Ash after Mechanical Activation

The chemical composition of coal fly ash is shown in Table 1. The coal fly ash used in this study was composed of the oxides of Si, Al, and various metals. Coal fly ash powder was mechanically treated by the attrition-type mill, and its morphology change was observed by the SEM. Figure 2 shows

the SEM images of the raw and MA coal fly ash powders. Coal fly ash was vitrified by quenching after the melting of aluminosilicate, which is an inorganic component in coal. Coal fly ash used in this study was also found to be made of spherical particles with a smooth surface (Figure 2a). The surface morphology of coal fly ash particles changed roughly by the mechanical activation (Figure 2b). From these SEM images, it can be seen that the mechanical treatment by the attrition-type mill does not cause the particles to be pulverized but only affects the surface morphology of the particles.

Table 1. Chemical composition of coal fly ash (mass %).

Products	Si	Al	Na	K	Ca	Fe	Mg
Coal fly ash	62.7	21.6	0.9	2.0	4.6	7.1	1.1

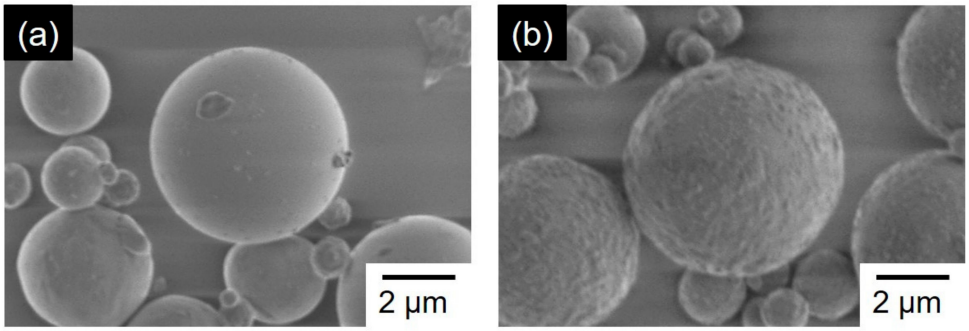

Figure 2. SEM images of coal fly ash (**a**) before and (**b**) after mechanical treatment.

The particle size distribution of the raw and MA coal fly ash powders is shown in Figure 3. The mean particle size (d_{50}) and the specific surface area of the samples are shown in Table 2. The mean particle size of raw, 10 min, 20 min, and 30 min MA coal fly ashes are 4.4, 4.7, 4.6, and 5.1 μm, respectively. The specific surface area of these are also 1.8, 2.2, 1.9, and 2.2 m^2/g, respectively. No grinding effect was found on the particle size. Mechanical activation by the attrition-type mill does not reduce the particle size of coal fly ash particles regardless of the treatment time. These results support that the coal fly ash particles are not ground in the mechanical treatment by the attrition-type mill and correspond well with the results from the SEM images in Figure 2.

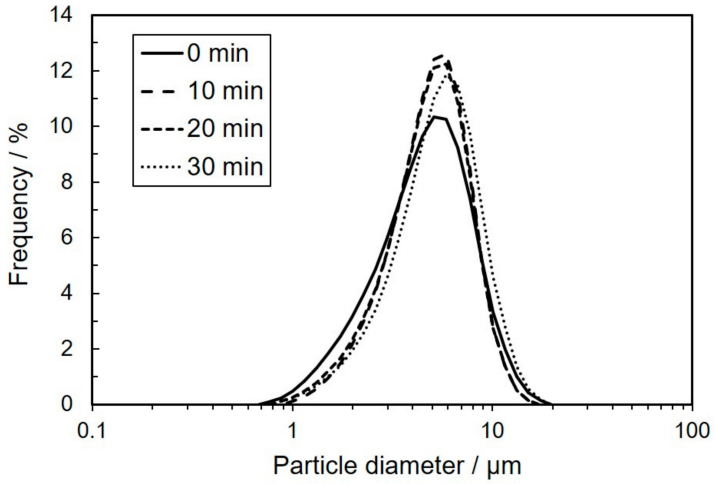

Figure 3. Particle size distribution of coal fly ash before and after mechanical treatment.

Table 2. Mean particle diameter of coal fly ash before and after mechanical treatment.

Characteristic	Mechanical Treatment Time (min)			
	0	**10**	**20**	**30**
Mean Particle size d_{50} (μm)	4.4	4.7	4.6	5.1
Specific surface area (m^2 $g^{-1)}$	1.8	2.2	1.9	2.2

The XRD patterns of the raw and MA coal fly ash powders are shown in Figure 4. The peaks of quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$) are confirmed in all the raw and MA coal fly ash powders. By activating coal fly ash by the mechanical treatment, any peak intensity is remarkably reduced, and a broad peak derived from the amorphous phase is confirmed [20]. Mainly the crystal phase and surface morphology of coal fly ash particles were changed by the mechanical treatment. No significant difference was found in powder characteristics, such as the particle size distribution and the specific surface area (Figure 3), before and after the mechanical treatment. The mechanical treatment under this condition makes the surface morphology rough and amorphous without changing the particle size. It is considered that this enhances the surface activity of coal fly ash and promotes the curing reaction of the geopolymer.

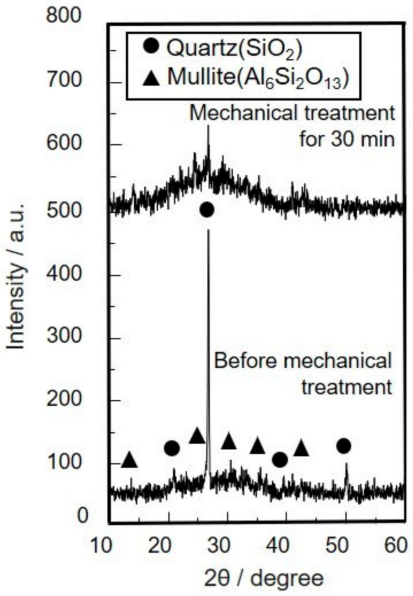

Figure 4. XRD patterns of coal fly ash before and after mechanical treatment.

The dissolution of Si^{4+} and Al^{3+} from coal fly ash is considered to be an index to show the effect of the mechanical activation. The dissolution amount of Si^{4+} and Al^{3+} were measured to evaluate the mechanical activation of the coal fly ash before the curing quantitatively. The raw and MA coal fly ashes were dissolved in 10 mol/L NaOH for 3 h, and then the concentration of Si^{4+} and Al^{3+} in the filtrate was measured after solid–liquid separation. Figure 5a,b shows the dissolution amount of Si^{4+} and Al^{3+} from coal fly ash, respectively. It was found that the dissolution amount of Si^{4+} and Al^{3+} increase as the mechanical treatment time increases. Although there were no changes in the specific surface area and particle size distribution (Table 2), the dissolution amount of Si^{4+} and Al^{3+} increased with an increase in the mechanical treatment time. These results are smaller than those reported previously [20] because the attrition-type mill does not increase the specific surface area. Therefore,

it is considered that the amorphization of the surface morphology of coal fly ash by the mechanical activation affects the dissolution of metal ions from coal fly ash.

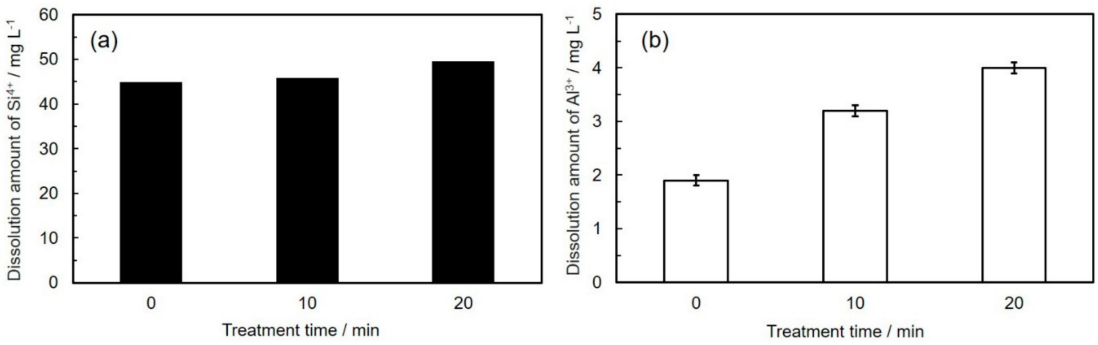

Figure 5. Dissolution amount of (**a**) Si^{4+} and (**b**) Al^{3+} ions from coal fly ash.

It is clarified from these results before curing operation that the mechanical activation affects the Si^{4+} and Al^{3+} dissolution from coal fly ash, suggesting that the promotion of dissolution makes the contribution to the reactivity of geopolymerization to increase the compressive strength and acid resistance.

3.2. Effect of Mechanical Activation on Compressive Strength of the Geopolymers

The compressive strength of geopolymers from raw coal fly ash under different curing conditions is shown in Table 3. For the sample obtained after 28 days of curing at 70 °C, the compressive strength of the sample shows 26.9 MPa. On the other hand, in the cases of 7 days at 70 °C and 28 days at RT, the compressive strength of the samples were 17.8 and 6.7 MPa, respectively. These values are smaller than the 26.9 MPa for 28 days at 70 °C. It appears that the mechanical properties of geopolymers using raw coal fly ash cannot be developed under mild curing conditions like low curing temperature at RT and a short time for 7 days.

Table 3. Compressive strength of geopolymers from raw coal fly ash under different curing conditions.

Curing Conditions	28 days–70 °C	7 days–70 °C	28 days–R.T.
Compressive strength (MPa)	26.9 (SD 4.0)	17.8 (SD 6.1)	6.7 (SD 2.2)

The compressive strength of geopolymers using the raw and MA coal fly ashes was shown in Figure 6. The curing conditions allowed it to stand for 28 days at 70 °C, 7 days at 70 °C, and 28 days at RT. For the samples obtained after 28 days at 70 °C, the compressive strength of geopolymers using the MA coal fly ash increased, and it shows 45.2 MPa for 30 min of treatment. This value is almost equivalent to the value reported previously [21]; however, the compressive strength can be increased under the optimized mechanical treatment conditions. In the case of 28 days at RT, the compressive strength of geopolymers using MA coal fly ash drastically increased with the increase in treatment time, and it shows 22.3 MPa for 30 min. It is found, however, that the compressive strengths of raw and 10 min remain very low under 20 MPa and that longer treatment time over 20 min is also required in the case of the RT curing.

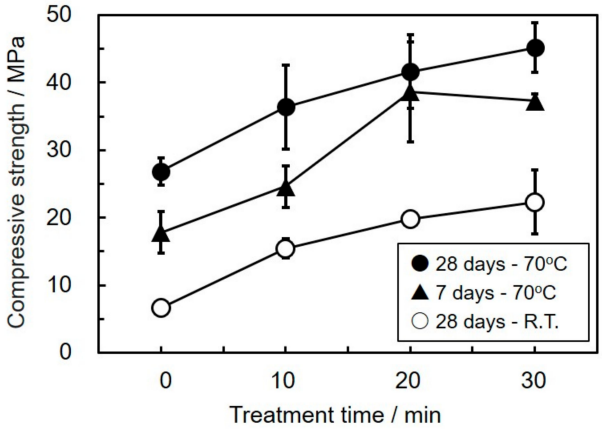

Figure 6. Correlation between the compressive strength of geopolymers under different curing conditions and mechanical treatment time.

For the samples of 7 days at 70 °C, the compressive strength also increased with the increase of treatment time. The value of 38.7 MPa can be obtained for 20 min of treatment time, and it is higher than 24 MPa as the standard endurance strength of general cement concrete. This result shows the possibility of shortening curing time. That is, even with a short curing time like 7 days, it is possible to get enough compressive strength.

The correlation between the compressive strength and the density of geopolymers were shown in Figure 7. Under mild curing conditions (curing for 7 days at 70 °C or 28 days at RT), the densification of the geopolymer was insufficient. The compressive strength tended to increase due to an increase in the density caused by the activation of coal fly ash particles by the mechanical treatment. The density effects on the compressive strength under milder curing conditions. In the curing 28 days at 70 °C, however, no correlation between the compressive strength and the density was shown in the same curing conditions. Under sufficient curing conditions, the density of the cured bodies becomes similar. It is suggested that the improvement of compressive strength is affected by the strength of bonding due to the mechanical activation of the particle surface.

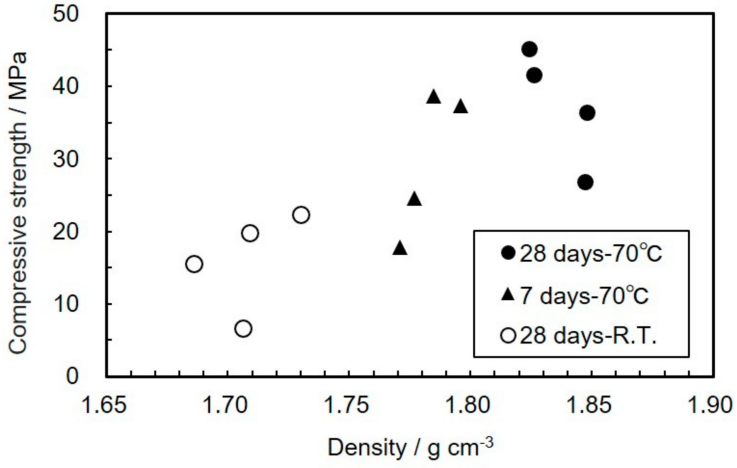

Figure 7. Correlation between density and compressive strength of geopolymers under different curing conditions.

The SEM images of the fracture surface of geopolymers from raw and MA coal fly ash aged at 70 °C for 28 days are shown in Figure 8. In the case of raw coal fly ash, unreacted coal fly ash particles remain a spherical shape, which would be the fracture origin for the strength decline of geopolymers [24]. On the other hand, a dense gel phase was observed for the samples of the MA coal fly ash [26]. It is

considered that the reactivity between the coal fly ash particles and the alkaline solution was improved by the mechanical activation. The improvement of strength is not only caused by the densification of geopolymer but also the disappearance of particle interfaces. Therefore, if the particle interfaces on the SEM disappeared by improving the reactivity of coal fly ash particles, the strength of geopolymers could be increased even under the mild curing conditions.

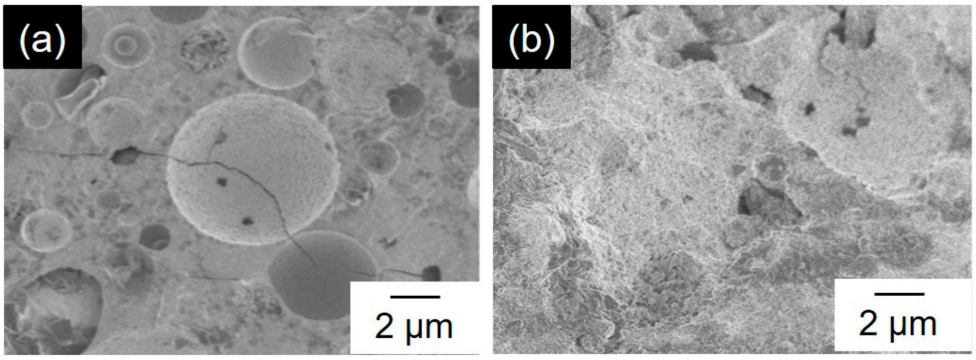

Figure 8. SEM images of the fracture surface of geopolymers from raw and MA coal fly ash for (**a**) 0 min and (**b**) 30 min at 70 °C for 28 days.

3.3. Acid Resistance Test of Geopolymers Cured from Mechanically Activated Coal Fly Ash

Geopolymers prepared from the MA coal fly ash were placed in 5 wt. % H_2SO_4 for 14 and 56 days. The changes in the shape of geopolymers were observed. The compressive strength of geopolymers was measured after the acid resistance test. Figure 9 shows an appearance of geopolymers obtained after 28 days of curing at RT after 56 days of the acid resistant test. From left to right, mechanical treatment times are 0, 10, 20, and 30 min, respectively. The hardened body using raw coal fly ash cannot keep its original shape after the acid immersion test. Whereas, the hardened body using MA coal fly ash can maintain their original shapes. It is considered that the improvement of acid resistance is also caused by the densification with the mechanical activation, as the same way of the compressive strength shown in Figure 6.

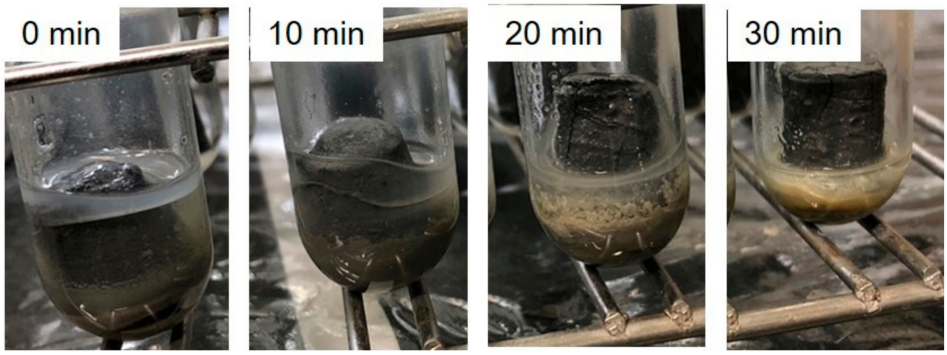

Figure 9. Appearance of geopolymers after 56 days of the acid resistant test: room temperature curing for 28 days. From left to right, mechanical treatment times are 0, 10, 20, and 30 min, respectively.

The compressive strength of geopolymers after an acid resistance test is shown in Figure 10. All the samples were obtained after 28 days of curing at 70 °C, then placed in 5 wt. % H_2SO_4 for 14 and 56 days. The samples of both the 14 days and 56 days show a tendency to increase the compressive strength as the mechanical treatment time increases. For the 56 days of acid immersing, the compressive strength using raw coal fly ash cannot be measured because of the collapse of the hardened body shape. On the other hand, both samples after 20 and 30 min show both about 23 MPa, respectively. These values are almost equivalent to the one without mechanical treatment before an acid resistance test. These results

indicate that not only the mechanical properties but also the acid resistance is improved at the same time by the mechanical activation.

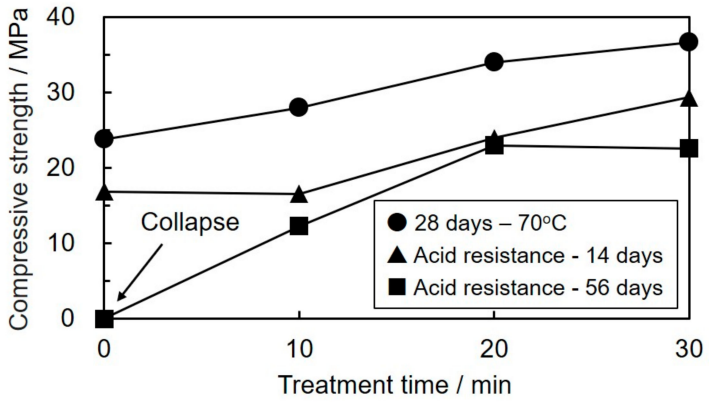

Figure 10. Compressive strength of geopolymers (28 days, 70 °C cured) from mechanically treated coal fly ash after acid resistant test (14 and 56 days).

4. Conclusions

In this study, coal fly ash was mechanically activated by using an attrition-type mill, which modifies only the surface morphology and the crystal structure of particles without decreasing the particle size. The mechanical activation improves the reactivity of coal fly ash during geopolymerization under milder curing conditions. The dissolution of Si^{4+} and Al^{3+} ions from coal fly ash increased after the mechanical activation. It is considered that the improvement of the compressive strength and the acid resistance are not only caused by the densification of the hardened body but also the disappearance of particle interfaces based on the high reactivity of coal fly ash particles. Thus, it is revealed that mechanical activation is effective for the fabrication of geopolymers with sufficient strength under milder curing conditions.

Author Contributions: M.M. and N.M. designed the study; K.Y. and K.O. prepared the samples; K.Y., K.O. and M.U. conducted the physical property measurements; M.N. advised; N.M. supervised; all authors participated in the discussion to interpret the results, and M.M. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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