Robust synthesis of coal bottom ash-based geopolymers using additional microwave heating and curing for high compressive strength properties

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Abstract−While coal bottom ash (CBA) contains an amount of amorphous silica and alumina as high as coal fly ash (CFA), its irregular particle shapes and excess unburnt carbon content compared to CFA are known to decrease the compressive strength of CBA-based geopolymers. Hence, we propose an advanced synthetic method of high-strength CBA-based geopolymer by appending microwave heating to conventional oven curing process without pretreatments for carbon removal. First, we blended finely crushed CBA with a moderate amount of 14 M NaOH alkali activator to make a mixture in a slightly wet state. Then, we fabricated precast samples by casting the mixture against 5-cm cubic molds with the help of a hand press. Next, the samples were hardened through the two-stage process of pre-dry-oven curing (12, 24 and 36 hr at 75 °C) and post-microwave-oven heating (up to 7 min under 700 W power). In essence, the specimens cured for 36 hr in the dry oven showed a considerable improvement in compressive strength just after being heated for 3 min in the microwave oven (from 12.8 to 40.5 MPa). This newly proposed synthetic method is proven to be very cost-effective for producing CBA-based geopolymer with high compressive strength.

Keywords: Coal Bottom Ash-based Geopolymers, Compressive Strength, Slightly Wet State, Microwave, Cost-effective Technique

INTRODUCTION

During the coal combustion process in coal-fired power plants, a large amount of coal combustion products (CCPs) are generated. CCPs are inorganic solid materials that are collected in emission control processes after coal is burned [1]. The global production of CCPs was estimated at more than 770 million metric tons in 2013, and it has grown continuously [2]. Coal fly ash (CFA) constitutes a major component of CCPs, followed by flue-gas-desulfurization gypsum, coal bottom ash (CBA), and boiler slag [3]. Among CCPs, CFA is a micro-sized powder with low bulk density, high water-holding capacity, and pozzolanic reactivity, which are favorable for industrial utilizations such as a concrete admixture and structural filling material [4,5]. Also, CFA has attracted great attention as a source material for geopolymers because of its high content of silica and alumina [6-8]. Geopolymers are cement-like binders with outstanding mechanical properties and eco-friendly characteristics, and can be synthesized by alkali-activation of aluminosilicate-rich materials like CFA [9,10]. In contrast, the utilization rate of CBA has not been as high as that of CFA even though it has almost the same chemical composition as CFA [2]. CBA has been less suited as a pozzolan or binder material because of its larger, irregular particle shape and higher content of unburnt carbon compared to CFA [1,2]. The irregular particle shape of CBA reduces its reactivity to an alkaline solution, so CBA-based geopolymer has hardly achieved a high compressive strength comparable to CFA-based geopolymer even after the particle size of CBA is made as small as that of CFA [11]. In addition, it has been reported that unburnt carbon residues as in CBA could deteriorate the compressive strength of geopolymers [12]. During activation of CBA under a strong alkaline environment, we found the carbon residues were readily dispersed into the blended media, and then floated upward to form a stratified streak of dark-stained phase at the upper part of each sample as the geopolymer paste got into curing process in a hot dry oven, which would result in preventing the development of a compressive strength in the geopolymer [13]. Lee et al. [14] showed that the compressive strength of briquette ash-based geopolymer was highly increased by using pulverized briquette ash with its most of unburnt carbon residues beforehand removed through a froth-flotation process where kerosene played the role of a carbon collector while pine oil acted as a frother. Thus, we can also expect the compressive strength of CBA-based geopolymer would be improved if the unburnt carbon remnants were got rid of from the received CBA before using it. However, if any carbon-removing process is applied for the unburnt carbons in CBA, it is certainly an annoyance because it will take many tedious, cumbersome tasks ahead of geopolymerization, as we can see in present techniques, including the water flotation method with collector and frother reagents [15], carbon-oxidization procedure in high temperature [16], gravitational separation through vibrating on inclined surfaces [17], and air agglomeration method within aqueous solution [18].

Accordingly, to fabricate high-strength geopolymers from CBA in a time- and cost-efficient manner, we propose a new synthetic method here. In the previous study [19], it was noticed that the negative effects of carbon remnants on the compressive strength of CBA-based geopolymers could be effaced by lowering the amount of

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water added to the source material as an alkali activator to keep the unburnt carbons from rising up during the geopolymer curing process. If the alkali activator is excessively supplied into CBA source material, the unburnt carbon particles embedded in CBA tend to dissolve out into the alkaline media and move upwards under the thermal-buoyancy effect in a hot dry oven. Then, the carbon remnants gather upside to make a new carbon-phase deposition at the top part of specimens during curing. This "carbon-phase separation" that occurs under alkali-solution rich environment later leads to weakening the compressive strength of CBA geopolymers [13]. Therefore, a well-limited amount of alkali-activator solution makes it possible for the dissolved unburnt carbons not to start to gather at the top part of CBA geopolymer specimens from the curing process [19]. Here, we used 14 M sodium hydroxide solution as an alkali activator to make CBA-based geopolymers at a well-controlled amount to maintain its mixture with the source material in a slightly wet state. Furthermore, we added a microwave irradiation step to the conventional curing process in a dry oven to achieve a high compressive strength in a short period. Microwave irradiation is an innovative heating method for the materials possessing dielectric molecules such as water. When the materials are exposed to a high-frequency alternating electric field, the entire volume is heated rapidly by molecular dipole rotation. Due to its fast and high volumetric heating characteristics, microwave energy promotes a dissolution of precursor species from source materials and facilitates a formation of reaction products; hence, the mechanical strength of geopolymers can be enhanced through microwave irradiation [20,21]. Despite the advantage of microwave energy, a rapid evaporation of water and high internal stress would be induced if the dielectric heating is too intensive, which in turn can lead to cracks and fractures in the hardened geopolymers. For this reason, researchers [20,21] suggested to limit a power of microwave irradiation at a few hundreds of watts or less to synthesize high strength geopolymers. However, in this study, because we have restricted the pouring amount of alkali activator into the CBA to a proper quantity, there is not so much water in our initial raw mixture to worry about the vigorous evaporation inducing fissures for a short time of the microwave heating, and thus we could employ microwave energy in an earlier stage of hardening process.

The aim of this study was to suggest a practically cost-effective synthetic method of CBA-based geopolymer with a high compressive strength in a comparatively short period of curing time. The geopolymer was synthesized from finely crushed CBA in a limited amount of 14 M NaOH solution with the aid of a 700 W household microwave oven for a few minutes soon after employing a conventional dry-oven curing process up to only one-and-a-half days. The effectiveness of this proposed method was verified with the high compressive strength outcomes according to the variations of dry-oven curing and microwave exposing times. Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) analyses were performed to examine the morphol-
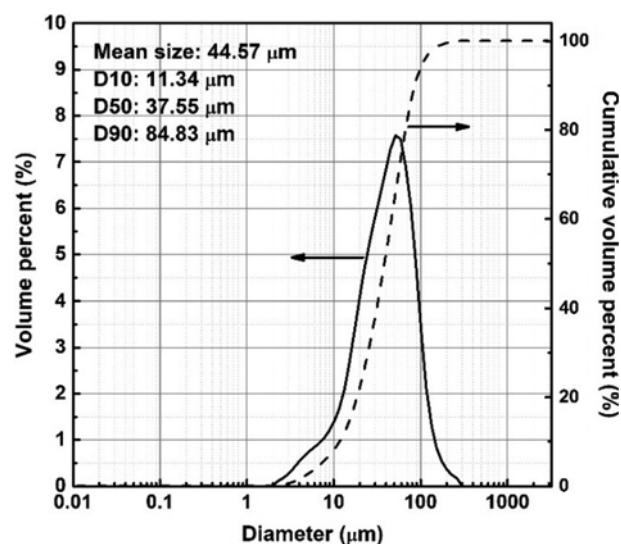

Fig. 1. Particle size distribution of crushed and sieved coal bottom ash (CBA).

ogy transition phenomena from this new technology application for the CBA-based geopolymer synthesis.

EXPERIMENT

1. Raw Materials

CBA was provided from Yeongheung power plant (South Korea). Because of its large particle size, the received CBA was crushed using a hammer mill, and sifted through a 200-mesh sieve. The particles that passed the sieve were used as source materials. The particle size distribution (LA-960, Horiba, Japan) of the sieved CBA showed a unimodal distribution with the mean particle size of 44.57 μm as given in Fig. 1. The chemical composition of CBA was determined by X-ray fluorescence (XRF) analysis with ZSK Primus II (Rigaku, Japan) in oxides, and loss on ignition (LOI) was measured following the procedure described in ASTM D7348. The percentages of components from XRF analysis were recalculated to total 100% including LOI. As shown in Table 1, the chemical composition of CBA is analogous to Class F fly ash (ASTM C618) because the sum of SiO_2, Al_2O_3, and Fe_2O_3 is larger than 70%. Fig. 2 shows the X-ray diffraction pattern (X'pert APD, PHILIPS, Netherland) of the CBA measured in a 2θ range from 5° to 70° with CuKα radiation. Even though the crystalline peaks of quartz and mullite are detected, the broad hump between $2\theta=15^\circ$ and 35° shows the presence of vitreous or amorphous phase in CBA, which would be involved in the geopolymerization reaction by being dissolved into the alkaline media and then condensing to form the reaction products [6].

2. Geopolymer Specimen Preparation

A sodium hydroxide solution was used as an alkali activator to

Table 1. Chemical composition of CBA

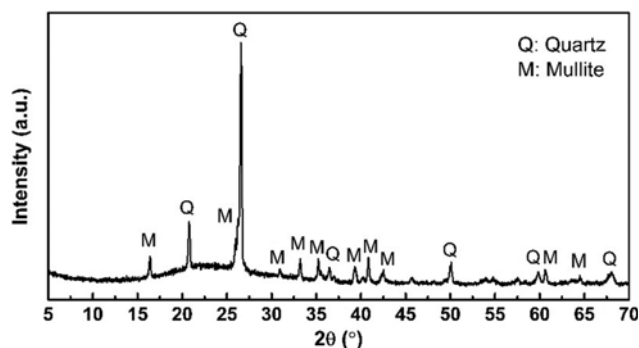| Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	TiO_2	LOI	Others
wt%	50.7	20.3	11.0	7.65	1.81	1.75	1.56	1.32	2.28	1.63

Fig. 2. X-ray diffraction pattern of CBA.

synthesize geopolymers. NaOH pellets (≥93% purity, Duksan, South Korea) were dissolved into tap water to make a 14 M concentration. After the NaOH pellets were fully dissolved, the solution was rested in an atmospheric condition at least 4 hours to release the heat generated from an exothermic NaOH dissolution process. The alkali activator was added to the sieved CBA until its mass ratio to CBA reached to a critical value (the mass ratio of L/S [liquid/solid]= 0.38), and then they were blended together in a Hobart mixer for 5 minutes at 60 RPM to make a homogeneous paste. At the given L/S ratio, which was determined from several preliminary experiments, the paste was in a damp state that behaved like a slightly wet clay soil. Due to the lack of mobility or fluidity of the paste, the unburnt carbon impurities in the source materials were not able to migrate to the top side of the samples during the curing process in a hot oven, as discovered in the previous study [19]. Furthermore, the amount of moisture content in each sample was not enough for the sample to be ruptured due to a rapid overheating expansion during its microwave irradiation even for several minutes, although the power level was much higher than those proposed in other researches [20,21]. From the preliminary experiments, when L/S ratio was greater than the critical value (0.38), the paste was not suitable to be used because it was not possible to prepare the precast samples, as well as the occurrences of carbon-phase separation and cracking during the hardening processes. In contrast, as the L/S ratio got less than the value, the compressive strength was incapable of developing to the high level due to the poor geopolymer reaction condition, i.e., low degree of alkali activation. As soon as the mixed paste was prepared, it was poured into 5-cm plastic cubic molds by applying compression force with a hand press machine. As the cubic-shaped precast samples were instantly demolded, they were put into a 75 °C dry oven for 12, 24 and 36 hours, respectively. The samples were wrapped in a plastic bag before being placed into the dry oven in order to keep the humidity high during the curing process. Otherwise, the samples would suffer from cracks due to the dry-shrinkage [22]. After the oven curing process, the samples were unwrapped, cooled to an ambient temperature, and then moved into a household microwave oven for the additional several-minute microwave heating under the power level of 700 W. The specimens cured for 12 hours were microwaved up to 7 minutes, while 24- or 36-hour-cured samples were for 5 minutes or less. If the microwave irradiation time exceeded the above-mentioned time ranges, the physical strength of

the samples became too fragile and even sometimes large cracks occurred, due to the overheating. Three identical samples were made at each fabrication condition for their test values to be averaged. The name of each sample was designated according to the applied durations of dry-oven curing and microwave treatment as follows:

○**H**□**M**

○=dry-oven curing time in hours (=12, 24, or 36).
□=microwave irradiation time in minutes (=0-7).

For example, 24H3M sample was cured in a dry oven for 24 hours, and then microwaved for 3 minutes.

3. Mass-loss Characterization, Compressive-strength Testing and Analysis

During the hardening processes of dry-oven curing and microwave heating, the precast geopolymer samples reduced in mass continuously as the water dried or evaporated from the samples. Because the water content of geopolymers has a close relationship with their compressive strength [23,24], it was required to measure the mass of the evaporated water. The reduced mass of sample was calculated in a relative percentage using the following equation:

$$\text{Mass loss } (\%) = \frac{m_i - m_f}{m_i} \times 100, \tag{1}$$

where m_i=initial mass of sample measured before going into the dry-oven curing process, and m_f=final mass measured when the sample was completely cooled to the ambient temperature after the microwave heating. The compressive strength of the cooled specimens was tested in accordance with ASTM C109 using a compression testing machine (PL-9700H, Woojin, South Korea). Next, to examine the microstructural characteristics and their changes according to the dry-oven curing and microwave irradiation times, scanning electron microscopy (SEM) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analyses were performed. For micro-morphological observation, SEM (Nova Nano SEM 200, FEI, USA) was employed to take the images of some broken samples after the compressive strength test. Because the raw material and geopolymer samples were electrically nonconductive materials, the specimens were coated with gold, and then the images were taken at 1.5 k magnification with 10.0 kV acceleration voltage. Also, to examine the transition in the bond structures of the main functional groups involved in the geopolymerization reaction, ATR-FTIR analysis (Frontier FT-IR Spectrometer, PerkinElmer, USA) was performed for raw CBA and powdered geopolymer samples. The spectra were recorded within a range of 4,000-400 cm⁻¹ in transmittance with a 4 cm⁻¹ resolution, but the results were represented within only 1,700-400 cm⁻¹ because there was no observation worth noting above 1,700 cm⁻¹ except a peak related to free water.

RESULTS AND DISCUSSION

1. Compressive Strength and Mass Loss

The compressive-strength values of CBA-based geopolymer specimens that were pre-cured in 75 °C dry oven for three different times of 12, 24 or 36 hours were measured according to the micro-
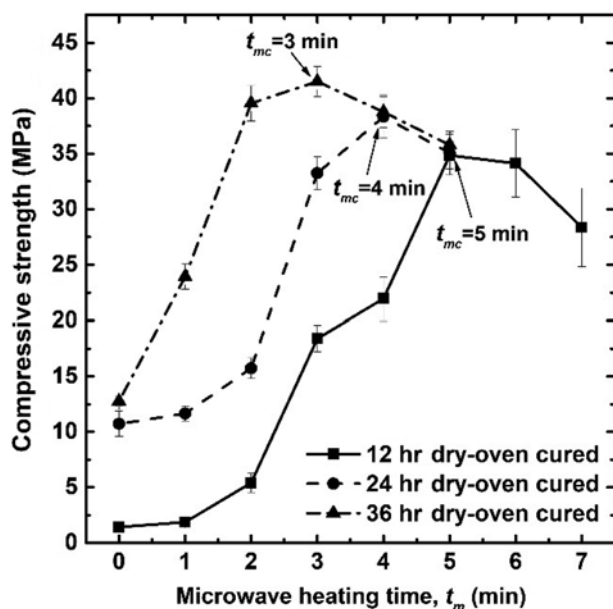
Fig. 3. Compressive strength results of CBA-based geopolymer samples (pre-cured in 75 °C dry oven for three different curing periods of 12, 24 and 36 hr, respectively) according to the microwave heating time (t_m). t_{mc} strands for the critical microwave heating time after which the compressive strength starts to decrease from its maximal value.
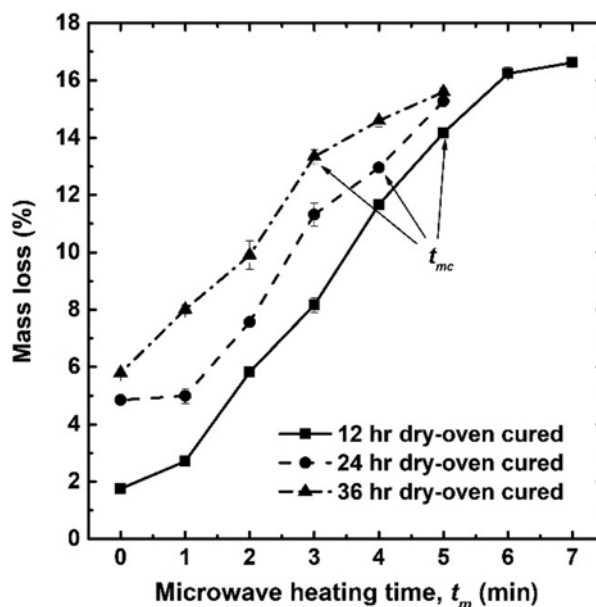

Fig. 4. Relative mass-loss curves of CBA-based geopolymer samples (pre-cured in 75 °C dry oven for three different curing periods: 12, 24 and 36 hr, respectively) according to the microwave heating time (t_m).

wave-irradiation time. The results are shown in Fig. 3. Before exposing the geopolymers to 700 W power of microwave, the maximum compressive strength of 12.8 MPa was obtained in the samples cured for 36 hours in the dry oven (refer to the highest value at t_m=0 in Fig. 3). As soon as the specimens were exposed to the microwave energy, their compressive strength increased along with the irradiation time (more rapidly in case of 36 hr dry-oven-cured sample than the others) to some extent, and then began to decrease after reaching their maximum values. The compressive strength was arrived at its highest value of 41.5 MPa in 36H3M sample which was three-times bigger than that in the sample without microwave exposure (i.e., 12.8 MPa in 36H0M sample). Also, 24 hr dry-oven-cured samples increased in the compressive strength by 3.6-times as a result of the microwave heating for 4 min (from 10.7 to 38.3 MPa as shown as the dashed line in Fig. 3). In 12 hr dry-oven-cured samples, the effect of microwave energy was more dramatic: their compressive strength just after 5 min of the microwave irradiation increased almost 25-times as much as that in case of no exposure to microwave (from 1.4 to 34.9 MPa as shown as the solid line in Fig. 3). Among other researches that utilized CBA as a source material of geopolymers without any microwave application, the geopolymer mortars synthesized by Chindaprasirt et al. [11] achieved its high compressive strength of 18 MPa after two days of dry-oven curing at 65 °C, and Topçu et al. [25] obtained the highest compressive strength of 26 MPa at one day for their geopolymer cements. Compared to these results, it has to be noted that much higher value of compressive strength was achieved only after 12 hr curing process in 75 °C dry oven followed by 5 min microwave irradiation. Moreover, the highest compressive strength developed here in 36H3M sample (41.5 MPa) was comparable to that of the geo-

polymer cured at ambient temperature for 28 days (45 MPa) in the research performed by Slavik et al. [26], where their fluidized-bed-combustion CBA source material had a final particle size below 10 μm and contained relatively larger CaO (17.9 wt%), which made it possible for their geopolymer samples to be solidified without any heat treatment.
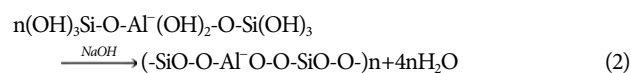
As the precast samples were subjected to the hardening process in the dry and microwave ovens, they were reduced in mass due to the water evaporation as seen in Fig. 4. The evaporation of water during the dry-oven curing was not so significant (refer to the values at t_m=0 in Fig. 4). The low extent of mass loss in this stage was directly related to the hardening environment of geopolymer samples, that is, the specimens were placed in a dry oven after tightly being sealed in a plastic bag in order to keep the dry-shrinkage in the wet paste and thus cracking from occurring [22]. As the geopolymer samples were exposed to an elevated temperature in the dry oven, water evaporated from the sample into the space confined in the plastic bag, and thus its air got saturated with the vapor, which prevented the moisture in the sample from escaping further. Considering the nominal water evaporation occurred in the dry oven, the improvement of the compressive strength in this stage was ascribed to the progress of the geopolymerization reaction rather than drying, which was well confirmed from the observations in the previous researches [27-29].

On the other hand, water rapidly evaporated from the geopolymer samples when they were exposed to microwave energy as the body temperature of the samples was actively elevated due to the vigorous dielectric heating. As shown in Fig. 4, the mass loss percentage rose beyond 15% when the 24 hr or 36 hr dry-oven-cured samples were heated in the microwave oven for only 5 min (or 6 min for 12 hr dry-oven cured samples). When we looked into

the compressive strength and mass loss results, the correlation between them could be observed as follows. For a few minutes of microwave heating, the compressive strength continued to increase as water evaporated from the samples. However, the mass loss percentage where all the samples had their highest values in compressive strength belonging to the region of 13-14% (refer to t_{mc} in Fig. 4), and beyond this range the compressive strength became deteriorated as shown in Fig. 3. Thus, there appeared an aspect of weakening rather than improving in the compressive strength after the critical microwave heating time (t_{mc}). This observation strongly suggested the correlation between the compressive strength of geopolymers and its water content.

The physical properties of geopolymers are highly influenced by water because it is an indispensable element in the geopolymer chemistry that plays roles of (1) a solvent of alkaline compounds (here, NaOH) to contain OH^- anion which is necessary to attack the source material, (2) a reactant in the dissolution and hydrolysis of silicate and aluminate species during the reaction, and (3) a reaction product that is re-generated at the polycondensation stage of those species [22]. The water that is uninvolved in the reaction or dissociated from the polycondensation of hydroxylated silicon/aluminum species is present as physically bonded or free water, whereas the water in the interstitial region of the matrix remains as chemically bonded water [30]. Even though the physically bonded water constitutes the majority of the entire water in geopolymer matrix, it has been reported that removing it does not cause any harm to the mechanical properties of the geopolymers [30]. Instead, the elimination of the water that regenerated from geopolymerization would result in the development the compressive strength of geopolymers because it promoted additional polycondensation reac-

tion as shown in the following equation [31].

$$n(OH)_3Si\text{-}O\text{-}Al^-(OH)_2\text{-}O\text{-}Si(OH)_3$$
$$\xrightarrow{NaOH} (\text{-}SiO\text{-}O\text{-}Al^-O\text{-}O\text{-}SiO\text{-}O\text{-})n + 4nH_2O \qquad (2)$$

Hence, the compressive strength of CBA-based geopolymers increased to a higher level after a few minutes of the microwave heating as the complementary geopolymerization reaction was stimulated so far as the microwave energy evaporated the regenerated water from the matrix.

However, the compressive strength of geopolymer did not increase proportionally to the specimen's exposure time in the microwave oven as aforementioned. There existed critical microwave-heating time (t_{mc}=3, 4 and 5 min for the samples precured in 75 °C dry oven for 36, 24 and 12 hours, respectively) after which the compressive strength started to decline from its maximal value as shown in Fig. 3. This transition seemed to have a relation to a convolution of thermal expansion and shrinkage that occurs in the geopolymer structure according to the extent of microwave heating time. Because of the intensive and penetrative heating characteristics of microwave, the body temperature of the geopolymer samples could rise to much above 200 °C from its center to surface in a few minutes of microwave irradiation [32,33]. Upon heating, not only physically bonded water that could easily dehydrate under a relatively low temperature range (ambient temperature to 100 °C), but chemically bonded water also would escape from the specimen as the temperature rose much higher than 100 °C [30]. After the mass loss percentage exceeded a certain level (=13-14%, refer to t_{mc} in Fig. 4), in turn, the samples experienced significant thermal shrinkage that would exert a high thermal stress on the internal structure, and it consequently led to the deterioration of the com-
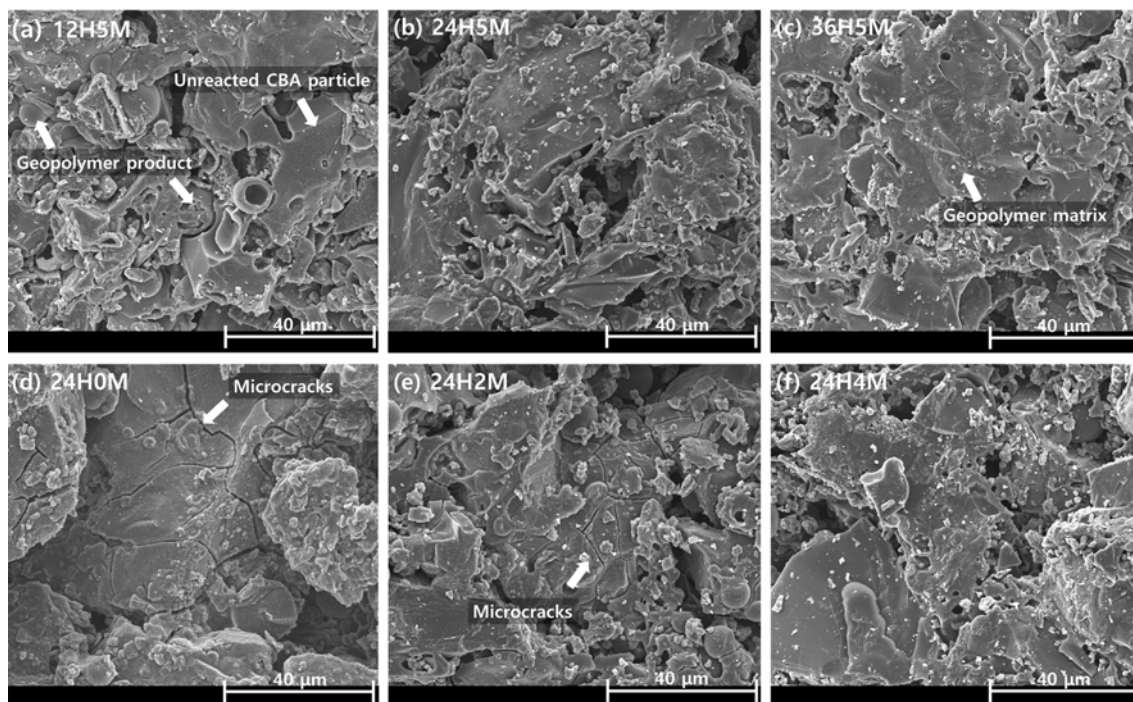

Fig. 5. SEM micrographs of geopolymer samples. (a), (b) and (c): after 5 min microwave irradiation for 12, 24 and 36 hr dry-oven cured samples, respectively. (d), (e) and (f): after 0, 2 and 4 min microwave irradiation, respectively, for 24 hr dry-oven cured samples.

pressive strength [34,35]. In addition, when the microwave heating time was much more extended from the range employed in the study, the internal thermal stress highly increased, and thus somewhat large cracks turned out on the front surfaces of the specimens.

2. SEM Analysis

It is important to observe the change in the micro-morphology of the geopolymers because the improvement of the microstructural homogeneity would lead to the development of their physical strength [36]. An SEM inspection was performed to examine the effects of dry-oven curing and microwave irradiation on the morphology of CBA-based geopolymers as given in Fig. 5. The images in the upper row (Fig. 5(a)-(c)) revealed the microstructural change related to the increase in the dry-oven curing time. The primary geopolymer products with spherical shape were observed in 12H5M sample in company with unreacted angular CBA particles, which indicated a lower degree of alkali activation because of the insufficient dry-oven curing (see Fig. 5(a)). As the samples were more exposed to the thermal treatment in the dry oven, the more homogeneous, denser geopolymeric matrix was formed because the CBA particles were more attacked by the alkali activator and involved in the reaction (see Fig. 5(b) and (c)), and this microstructural change might contribute to the development of the compressive strength [36]. The morphological changes resulting from the microwave irradiation are suggested in Fig. 5(d)-(f). The SEM image of the non-microwaved sample showed many microcracks over the whole structure (see Fig. 5(d)). When CBA-based geopolymer samples were exposed to the elevated temperature at 75 °C, non-uniform thermal expansion occurred in the matrix due to local variations in composition and temperature, inducing thermal stresses to arise cracking [37]. Yet, these cracks were observed to disappear gradually as the samples were exposed further to the microwave energy (see Fig. 5(d)-(f)), which led to the improvement of the compressive strength. This kind of crack-recovery could be explained from the compaction of microstructure that was reported to occur while the geopolymer samples were heated to about 200 °C [35]. Also, the additional reaction that was promoted by microwave energy we discussed earlier might be partially responsible for this crack-recovery phenomenon. However, micro-morphological changes related to the weakness inception in compressive strength after t_{mc} were not identified here under the SEM inspection. Thus, further study is required to elucidate the correct reasons in the morphological aspect.

3. ATR-FTIR Analysis

FTIR is a convenient tool not only for the qualitative analysis of structural characteristics in molecular level, but also to quantify the concentration of each chemical functional group within the sample, so it has been widely used for the structural analysis of aluminosilicate materials [24,30,38-42]. Especially, ATR-FTIR is very simple method for the analysis of solid-state materials in that it does not require any preparation procedure except for grinding the sample. Fig. 6 shows the FTIR spectra of CBA source material and geopolymer samples treated for 5 minutes in the 700 W microwave oven after being cured in the dry oven for 12, 24 and 36 hours, respectively. The broad, intense peak in a range of 800-1,200 cm^{-1}, which is ascribed to T-O (T=Al or Si) asymmetric stretching vibrations, was detected in both CBA and geopolymer samples [30]. In
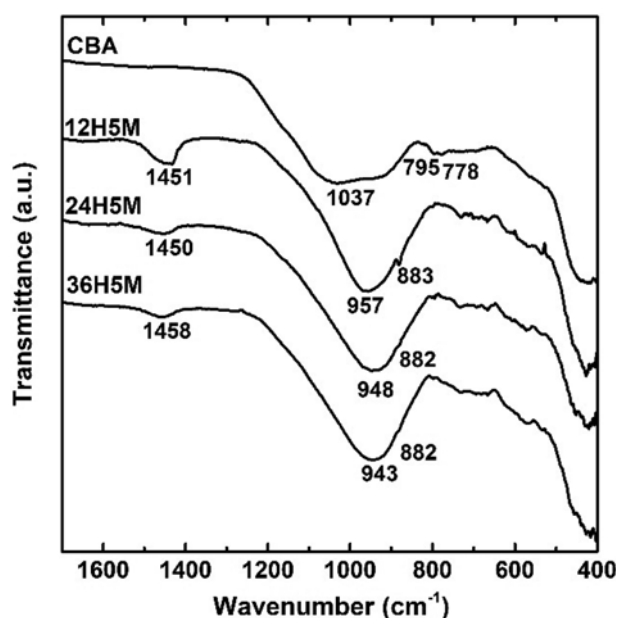

Fig. 6. FTIR spectra of CBA source material and CBA-based geopolymer samples heated in 700 W microwave oven for 5 minutes after being cured in 75 °C dry oven for 12, 24 and 36 hours, respectively.

the spectrum of the raw material, this peak was very broad and did not show distinct peaks, and this pattern displayed a highly disordered aluminosilicate structure of CBA [39]. After the geopolymerization, the wavenumber of this peak moved toward a lower value (from 1,037 to 957 cm^{-1} or below), demonstrating the obvious change in the microstructure, and hence, this peak has been called a "fingerprint" for the geopolymeric matrix [30,38]. Also, it was observed that the wavenumber of this peak decreased with the increase in the dry-oven curing time as presented in Fig. 6, which indicated that the energy state of the bond moved to the lower level. Given that the bond energy of Al-O is weaker than that of Si-O, this change in T-O asymmetric stretching bond structure can be interpreted in two ways: (1) reduction in the degree of silicate polymerization, and (2) incorporation of aluminum into silicate polymeric structures (i.e., replacement of SiO$_4$ species by AlO$_4$ in the polymeric structure) [30,38,40,41]. When the aluminosilicate source material is attacked by the alkali activator, aluminate species are more readily dissolved into the media at the beginning, and then the dissolution of silicate species increases gradually over time [40]. As the alkali activation proceeds, therefore, Al-rich geopolymeric structures are formed at the early stage of the reaction while the original amorphous silicate structures (from the source material) are dissolved into the alkaline media simultaneously, and thus the wavenumber of the fingerprint peak moves to a lower value, accompanying the development of the compressive strength [41,42]. After the activation of the source material is completed, in turn, the transformation in the geopolymeric gel structure would occur where the Al-rich phase evolves into Si-rich phase, and it leads to the re-increment in the wavenumber of the geopolymeric fingerprint peak, as well as the further strength gain [40-42]. In this regard, the decrease in the wavenumber of the fin-

gerprint peak in this study suggested that the activation of CBA was not completed but proceeding up to one and a half days of the oven-curing process, and it resulted in the development of the compressive strength.

From the spectra of all geopolymer samples, the peaks ascribable to the atmospheric carbonation of excessive sodium were detected near 1,450 and 883 cm^{-1} [24,43]. The intensities of these peaks were observed to decrease according to the increase in the dry-oven curing time, and this observation suggested that the geopolymerization proceeded further with consuming more sodium before it was carbonated by atmospheric CO_2. The peaks related to the presence of free water, which would be found at around 3,450 and 1,650 cm^{-1} [24], were not detected after 5 minutes of the microwave irradiation. This observation represented that most of the evaporable water in the samples was removed only after 5 minutes of the vigorous microwave heating under 700 W power level as we have seen in Fig. 4.

FTIR analysis was also performed for the samples that were microwaved for different minutes after the identical dry-oven curing period (the results are not presented here). It was observed that the intensities of the peaks related to free water and sodium carbonate were decreased with the increase in the microwave irradiation time, which demonstrated the more water evaporation and sodium consumption corresponding to the longer microwave heating. However, the consistent changes in the aluminosilicate structures resulting from the microwave irradiation were not clear from the FTIR results. To confirm whether the microwave energy could affect the chemical structure of CBA-based geopolymer, it is necessary to conduct further research.

CONCLUSION

We have proposed a cost-effective synthetic method representing high strength CBA-based geopolymers without any carbon-removal pretreatment of CBA in a comparatively short period of curing time. Because of the large, irregular particle shape of received CBA, the source material was prepared by crushing and sifting it to reduce the particle size. Then, 14 M NaOH activator was added to CBA source material until L/S ratio reached 0.38, at which the geopolymer specimens did not suffer from carbon-phase separation nor cracking during the hardening process. The blended geopolymer paste was cast against 5-cm cubic molds with the aid of a hand press machine and then detached from the molds immediately. Thereafter, the prepared precast samples were exposed to the combined hardening process of pre-dry-oven curing (for 12, 24 or 36 hr at 75 °C) and post-microwave-oven heating (up to 7 min under 700 W power). According to the variations of the dry-oven curing and microwave irradiation times, the reduced mass and compressive strength of the test samples were measured. Also, SEM and FTIR analyses were performed to examine the structural changes resulting from the different hardening conditions. The conclusions are the following:

(1) The CBA-based geopolymers fabricated via the proposed synthetic method attained outstanding compressive strength within a short time. The highest compressive strength of 41.5 MPa was obtained when the samples were cured in a dry oven for 36 hr and then exposed to microwave energy for 3 min. Also, 24 hr and 12 hr dry-oven-cured samples achieved 38.3 and 34.9 MPa, respectively, when each of them was heated in the microwave oven for 4 and 5 min.

(2) The microwave energy rapidly enhanced the compressive strength of geopolymer samples pre-cured in dry oven by additionally eliminating free and regenerated waters evolved from the geopolymer reaction for some appropriate irradiation times. With the help of the microwave oven, 24 hr and 36 hr dry-oven cured samples increased in their compressive strength more than three times. However, in 12 hr dry-oven cured sample, even though the effect of microwave irradiation on its strength was most prominent (i.e., the compressive strength increased about 25 times when compared to one without appending the microwave energy), its compressive strength did not show the maximal value in our experiment, which implies sufficient curing period for the alkali-activation of CBA in the dry oven is required before applying the microwave energy as discussed in ATR-FTIR analysis.

(3) The over-irradiation by microwave, however, caused excessive evaporation of structural water to induce the thermal expansion/shrinkage and high internal stress, which in turn led to a significant decrease in the compressive strength and even cracks. Thus, microwave heating should be employed so far as it would not cause the overheating in order to prevent the deterioration of the physical strength.

ACKNOWLEDGEMENT

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