

Microstructure evolution and mechanical properties of calcined kaolin processing waste-based geopolymers in the presence of different alkali activator content by pressing and casting

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Received date: 7 May 2020 Revised date: 22 April 2020 Accepted date: 23 July 2020

Keywords: Calcined kaolin processing waste Geopolymers with low and high contents of alkali activator Microstructure evolution Mechanical properties Pressed and cast geopolymers

Abstract

In this work, microstructure evolution and mechanical properties of calcined kaolin processing waste-based geopolymers in the presence of low and high contents alkali activators were studied. Lower and higher contents of alkali activators were employed to synthesize geopolymers by pressing and casting methods, respectively. Chemical bonding analysis, microstructure/elemental analysis, phase composition analysis, and compressive strength test were performed using FTIR, SEM/EDX, XRD, and universal mechanical testing machine, respectively. Findings showed that geopolymer with the low content of alkali activator formed by pressing (pressed geopolymer) might promote in the higher degree of geopolymerization because of higher compacted matrices but geopolymer with the high content of alkali activator formed by casting (cast geopolymer) would hinder the degree of geopolymerization reaction. Microstructure of pressed geopolymer showed a denser structure, no cracks, and lower porosity in comparison to the cast geopolymer. The geopolymers contained the lower and higher contents of alkali activators resulted in the formation of geopolymeric gels, and of sodium carbonate, sodium hydroxide, and zeolite phases, respectively. Compressive strength of pressed geopolymer was approximately 24.39% higher than that of cast geopolymer. Highest compressive strength values of pressed and cast geopolymers were 27.74 and 22.30 MPa, respectively. Thus, pressed geopolymer contained a lower content of alkali activator and had higher compressive strength in comparison to the cast geopolymers contained a higher content of alkali activator.

1. Introduction

Geopolymers are a three-dimensional aluminosilicate material which are in amorphous form. It can be synthesized by mixing aluminosilicate-based raw materials with a strong alkali activator (e.g., alkali hydroxide and silicate solutions) at low or ambient temperatures [1]. When the aluminosilicate raw material reacts with a strong alkali activator, geopolymerization occurs. Geopolymerization refers the dissolution of aluminosilicate species in alkali activator to form an amorphous three-dimensional aluminosilicate network structure via a polycondensation reaction [2,3]. Geopolymers are considered a new green construction material which is environmentally friendly and low carbon dioxide emission due to the use of by-products and waste from industry as an aluminosilicate source. In contrast, they have excellent strength, fire resistant, chemical resistant properties and lower shrinkage [4,5] due to unique three-dimensional network structure. Compressive strength is an important goal in evaluating the mechanical properties of geopolymer. Normally, the indicator for success of geopolymerization process is the value of mechanical strength and the densification of microstructure of geopolymers. These properties attract the attention of many researchers in the field of construction. Therefore, both mechanical properties and microstructure are influenced by many parameters such as liquid or solid contents [6,7], the proportions of reactive phases [7], the chemical composition [8], types of aluminosilicates [9], alkali silicates and alkali hydroxides [10], alkali concentration [11], and curing times [12].

However, one key factor affects the mechanical properties and microstructure of geopolymers is the forming method. Normally, if geopolymer is formed by casting method, it still uses high amount of alkali activator. The geopolymer is produced from high content of alkali activator by casting method, resulting in the hindering degree of geopolymerization reaction and the formation of CO_3^2 group in the geopolymer system having low mechanical

properties. At the present, this work is fabricated geopolymer with low content of alkali activator by pressing method. The advantage of pressing method can reduce the amount of alkali activator in the preparation process of geopolymers by pressing, and improve the mechanical strength and microstructure compared to casting. Moreover, the pressing method is a common method for tile and brick productions, but this method is rarely found in geopolymer production and the published research literature.

The purpose of this work was to study the microstructure evolution and mechanical properties of calcined kaolin processing waste-based geopolymers in the presence of low and high contents of alkali activators. The geopolymer samples were synthesized with lower (20-26 wt%) and higher (46-52 wt%) contents of alkali activators by pressing and casting methods, respectively. The mechanisms of microstructure evolution were investigated by SEM, FTIR, and XRD results. The microstructure evolution and mechanical properties were discussed by geopolymerization reaction of the geopolymers with the low and high contents of alkali activators by comparing between pressing and casting methods. Additionally, bulk density, the water absorption, and apparent porosity of geopolymers were used to describe comparisons with the microstructure and mechanical properties.

2. Experimental

2.1 Preparation and characterization of raw materials

Calcined kaolin processing waste was produced via calcination at 700°C in air for 1 h [13] in the electric furnace (HP Advanced Ceramic Company Limited, Thailand); a heating rate of 2°C·min⁻¹ was used. The XRD patterns (X'Port Pro, PANalytical) of the kaolin processing waste and the calcined kaolin processing waste are shown in Figure 1. The kaolinite and halloysite phases disappeared after calcination at 700°C because of the complete dehydroxylation and transformation of kaolin (kaolinite and halloysite) to metakaolin (metakaolinite and metahalloysite). In addition, the intensities of the muscovite, mica, and sanidine crystalline phases decreased after calcination because of the state of disorder. The chemical components (S8 Tiger, Bruker) of the calcined waste are presented in Table 1. The particle size and average density of calcined kaolin processing waste were 63.83 μ m (D (0.5)) and $2.62 \text{ g} \cdot \text{cm}^{-3}$.



Figure 1. XRD diffractograms of kaolin processing waste and calcined kaolin processing waste.

Table 1. Chemical components of kaolin processing waste and calcined kaolin processing waste.

Component	Kaolin processing waste (wt%)	Calcined kaolin processing waste (wt%)
SiO ₂	51.21	56.56
Al ₂ O ₃	30.98	33.85
Na ₂ O	0.02	0.23
K ₂ O	5.20	5.15
CaO	0.02	0.05
MgO	1.19	0.05
TiO ₂	0.16	0.16
Fe ₂ O ₃	2.22	2.16
MnO	0.15	0.14
SO ₃	-	-
LOI	8.85	1.65
Total	100.00	100.00

NaOH flakes (98% purity) were purchased from PT. Interchem Plasagro JAYA, Indonesia. The Na₂SiO₃ solution was supplied from C. Thai Chemical Company Limited, Thailand. The composition of the Na₂SiO₃ solution consisted of 31.25% SiO₂, 14.25% Na₂O, and 54.5% H₂O by weight, with an average specific gravity of 1.53 g·cm⁻³ (at 20°C). For the preparation of alkali activator, Na₂SiO₃ solution was mixed with NaOH (10 M) solution at room temperature for 1 h. The ratio of Na₂SiO₃ solution/NaOH solution were 2.25 by weight.

2.2 Preparation of geopolymers

The geopolymer samples were prepared using lower and higher contents of the alkali activators by

pressing and casting methods as shown in Figures 2(a) and 2(b), respectively. The synthesis conditions for the geopolymers are shown in Table 2.

For the geopolymer semidry powder preparation via the pressing method, the calcined waste was mixed with the lower content of alkali activator for 5 min in a Hobart mixer; the alkali activator comprised between 20-26% of the total sample weight. The resulting semidry powders were poured in the cylindrical stainless-steel mold with a diameter of 25 mm. These semidry powders were pressed via the hydraulic pressing machine at 20 MPa to obtain a specimen with a height of 50 mm.

Methods	Liquid/solid	Na2SiO3/NaOH	Mixture proportions (wt%)			
			Calcined kaolin processing waste	Alkali activator		
Pressing	0.25	2.25	80	20		
	0.28	2.25	78	22		
	0.32	2.25	76	24		
	0.35	2.25	74	26		
Casting	0.85	2.25	54	46		
	0.92	2.25	52	48		
	1.00	2.25	50	50		
	1.08	2.25	48	52		

Table 2. Ratios of mixture proportion.

*Liquid/solid ratio (Liquid is the alkali activator in weight and solid is the calcined kaolin processing waste in weight)



Figure 2. Geopolymer samples produced from low and high contents of alkali activator by (a) pressing and (b) casting methods, respectively.

For the geopolymer paste preparation via the casting method, the calcined waste was mixed with the higher content of alkali activator for 5 min in a Hobart mixer; in this case, the alkali activator comprised between 46-52% of the total sample weight. The pastes were poured in silicone mold with dimension of $50 \times 50 \times 50$ mm and was then oscillated on the vibrating table for 5 min. The sample remained in the mold for a further 24 h prior to demolding.

Following the demolding of the samples, they were covered with plastic film to prevent water evaporation and kept at room temperature for 7 days ± 3 h, according to ASTM C109/C109M-02 [14].

2.3 Testing and characterization of geopolymers

The water absorption, apparent porosity, and bulk density of synthesized geopolymers were measured according to ASTM C20-00 [15]. FTIR spectrometry (Spectrum One, Perkin Elmer) was employed to measure the Si-O-Al and Si-O-Si bonds in the geopolymer structure. FTIR results of geopolymer powders were recorded in the range of 400-4000 cm⁻¹ and the instrument has the resolution of 4 cm⁻¹. Field emission scanning electron microscopy (FESEM) was used to observe the microstructure of the geopolymer sample fracture surfaces. The geopolymer samples were coated with gold before examination by SEM and the chemical composition was measured by energy dispersive X-ray spectroscopy (EDX). The phase compositions of hardened geopolymer powders were examined using X-ray diffraction (XRD) (X'Port Pro, PANalytical) and Cu Ka radiation in order to identify the phase component of materials. XRD diffractograms were recorded in range of 5-80° at step size of 0.02°. The compressive strength of the geopolymer samples was determined using a universal mechanical testing machine. Seven samples of each formula were tested to assess the strength and the highest and lowest compressive strength values were disregarded before determining the average compressive strength.

3. Results and discussion

3.1 Water absorption, bulk density and apparent porosity of geopolymers

Table 3 shows the water absorption, bulk density and apparent porosity of pressed and cast geopolymers. The increasing content of alkali activator caused a significant decrease in the water absorption of the pressed geopolymer. In contrast, the water absorption of the cast geopolymer increased with increasing content of alkali activator. The water absorptions of pressed and cast geopolymers were in the ranges of approximately 14.15-16.70% and 19.21-21.36%, respectively.

The bulk density of the pressed geopolymer slightly increased with increasing content of alkali activator. On the other hand, the bulk density of cast geopolymer slightly decreased with higher content of alkali activator. Bulk densities of 1.63-1.69 g·cm⁻³ and 1.45-1.50 g·cm⁻³ were obtained for the pressed and cast geopolymers, respectively.

The apparent porosities of the pressed and cast geopolymers increased and decreased, respectively, with increasing content of alkali activator. The apparent porosities of the pressed and cast geopolymers were 25.76-30.14% and 36.74-40.85%, respectively. The apparent density is related to both the water absorption and the bulk density.

Geopolymer with the lower content of alkali activator fabricated by pressing was compared to geopolymer with the higher content of alkali activator fabricated by casting. The pressed geopolymer exhibited lower water absorption and apparent porosity than the cast geopolymer. On the other hand, the bulk density of the pressed geopolymer was higher than that of the cast geopolymer. Therefore, the pressing method has a greater effect on the formation of pores in geopolymer samples. These results affected the microstructure and compressive strength and agree with the finding from other studies [16,17].

Table 3. Water absorption, bulk density and apparent porosity of geopolymers with low and high contents alkali activators formed by pressing and casting methods.

Physical properties in average values	Pressed	geopolym	ier		Cast ge	opolymer		
	Lower content of alkali activator (wt%)				Higher content of alkali activator (wt%)			
	20	22	24	26	46	48	50	52
Water absorption (%)	16.70	14.76	14.35	14.15	19.21	19.24	19.89	21.36
Bulk density (g·cm ⁻³)	1.63	1.68	1.69	1.68	1.49	1.50	1.48	1.45
Apparent porosity (%)	30.14	26.76	25.76	26.11	37.10	36.74	37.77	40.85

3.2 FTIR analysis of geopolymers

Figures 3(a) and 3(b) illustrate the FTIR spectra of pressed and cast geopolymers after the geopolymerization reaction. The pressed and cast geopolymers show Si-O-Al and Si-O-Si vibrations in the ranges of approximately 1011-1014 cm⁻¹ and 1008-1012 cm⁻¹, respectively. These are characteristic of the asymmetric stretching vibrations of Si-O-Al and Si-O-Si bonds of the AlO₄ tetrahedral and SiO₄ tetrahedral groups in the geopolymer network structure. These bands shift toward lower frequencies with increasing content of alkali activator, this shift is associated with increasing content of Al3+ incorporated in the SiO₄ tetrahedral forming the Si-O-Al stretching vibrations [18,19]. Moreover, these peaks present a broad band with increasing content of alkali activator, which can be ascribed to the formation of an amorphous phase during geopolymerization.

Comparing the FTIR results of the pressed and cast geopolymers, pressed geopolymers exhibit boarder peak of Si-O-Al and Si-O-Si groups rather than cast geopolymers. These board peaks can support to the higher occurrence of the amorphous phase of geopolymerization product. Thus, pressed geopolymers with lower or optimum alkali activators may result in the higher degree of geopolymerization due to higher compacted matrices (closeness of particles). In contrast, this work believed that the massive content of alkali activator in cast geopolymer will hinder the degree of geopolymerization reaction, resulting in the decrease in board peak. At high alkali activator, the excess water hinders the polycondensation kinetics resulting in smaller reactivity. Furthermore, excess water may dilute the reaction and then leach the more soluble ions and these ions could move them away from the reaction zone [20,21].

Moreover, only the cast geopolymer exhibits O-C-O vibrations from the CO_3^{2-} group at 1386-1395 cm⁻¹. These bands are associated with O-C-O stretching because of atmospheric carbonation, and suggest the formation of carbonated species in the geopolymer

samples [22-24]. The O-C-O vibrations do not appear in the pressed geopolymer because of the lower content of alkali activator. Pandey et al. [25] reported that the occurrence of $CO_3^{2^2}$ groups from carbonation impacts the compressive strength of geopolymers.



Figure 3. FTIR spectra of geopolymers with low and high contents of alkali activators formed by (a) the pressing and (b) the casting methods.

3.3 SEM observation and XRD analysis of geopolymers

Figure 4 presents SEM micrographs of pressed geopolymers with different contents of alkali activators. The microstructure of the pressed geopolymers indicated either voids or unreacted materials on fracture surfaces of the samples. The fracture surfaces of pressed geopolymers with alkali activators of 24 and 26 wt% were denser than pressed geopolymers with alkali activators of 20 and 22 wt%. Figure 5 shows a gel-like phase on the unreacted materials of the pressed geopolymer samples. From the EDX analysis, the gel-like phase on the unreacted materials consisted of Si, Al, Na, K, Fe, and O. The proportions of Si, Al, and Na were different in the gel-like phase of the pressed geopolymer samples

with different contents of alkali activator. The contents of Al and Si fluctuated, and the content of Na increased with increasing content of alkali activator. In this research, the gel-like phase on the unreacted materials was believed to be a geopolymeric gel. According to Heah [6], geopolymeric gels mainly consisted of Si, Al, and Na, which is similar to the composition derived from SEM/EDX analysis in this study. Moreover, it can be observed that the content of geopolymeric gel increased with increasing contents of alkali activators up to 26 wt%. The geopolymeric gel is capable of filling in the pores of the pressed geopolymer samples, which leads to the formation of denser microstructures [26,27]. Therefore, the dense microstructures and higher geopolymeric gel contents of the pressed geopolymers are clearly related to the compressive strengths measured for these materials.

Figure 4. SEM micrographs of geopolymer with low content of alkali activator formed by pressing method.

Element wt% Element wt% 29.74 31.59 Ο Ο Si 34.76 Si 34.52 Al 19.46 21.04 Al 1.78 2.59 Na Na Κ 8.42 Κ 7.72 Fe 5.84 Fe 2.54 Total 100.00 Total 100.00 10 un 10 un Alkali activator = 20 wt% Alkali activator = 22 wt% Element Element wt% wt% Ο 48.15 0 50.76 Si 20.82 Si 22.84 Al 15.32 Al 15.43 Na Na 3.83 4.44 Κ 4.88 Κ 3.4 Fe Fe 7.02 3.13 100.00 100.00 Total Total

Alkali activator = 20 wt%

Alkali activator = 22 wt%

Figure 5. SEM micrographs and EDX results of geopolymeric gel in geopolymer with low content of alkali activator formed by pressing method.

The microstructure of cast geopolymers indicated unreacted materials, crystals, and cracks on the fracture surfaces of the samples, as shown in Figure 6. Moreover, the fracture surfaces of the geopolymers presented seed-like crystals, hexagonal plate crystals, and white crystals, as illustrated in Figure 7. The seedlike crystals were observed in SEM images for all the cast geopolymer samples and EDX analysis indicated the crystals were rich in Si, Al, Na, and O. The seedlike crystals were believed to be the crystalline phases of zeolite X. In cast geopolymer samples with 46 and 48 wt% alkali activators, the seed-like crystals had irregular shapes; this phenomenon was assumed to be associated with the initial growth stage of zeolite X. In the cast geopolymer sample with 50 wt% alkali activator, the zeolite X formed complete octahedral crystals. Cast geopolymers with 52 wt% alkali activator indicated octahedral crystals (zeolite X), hexagonal plate crystals, and white crystals. The hexagonal crystals were rich in Si, Al, Na, and O, and the white crystals were rich

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in Na, C, and O. The hexagonal crystals were similar to the alkali earth hydroxide-like phase in cement [28] and believed to be crystalline phases of NaOH. The white crystals were assumed to be the crystalline phases of Na₂CO₃ [29]. The crystalline phase of zeolite X (Na₉₂ (Si100Al92O348), JCPDS card No. 89-8253) was related to the XRD results, as shown in Figure 8. However, NaOH and Na₂CO₃ were not detected by XRD though the presence of Na₂CO₃ was confirm by FTIR. Na₂CO₃ is a carbonation product formed in the presence of high Na⁺ contents. Therefore, for the cast geopolymers, produced with high proportions of alkali activator, the high Na⁺ content readily promotes efflorescence (the formation of Na₂CO₃) [21]. In addition, cracks were observed via SEM analysis in cast geopolymer samples. The cracks observed in the cast geopolymers produced with higher proportions of alkali activator were larger than the cracks in the pressed geopolymers produced with lower content of alkali activator. The crack of geopolymers was triggered via shrinkage during the curing process and the compressive load for breaking samples. The number of cracks and the effect of sodium carbonate resulted in a reduction of the compressive strength for the geopolymers.

Figure 9 compares the SEM microstructures of geopolymers with the low and high the alkali activators formed by pressing and casting, respectively. Cracks were not found in the pressed geopolymers with different contents of alkali activator. In contrast, the cast geopolymers showed macro cracks and higher crack densities when the proportion of alkali activator was increased. Additionally, the pore contents of the pressed geopolymers were less than those of the cast geopolymer.



Alkali activator = 50 wt%

Alkali activator = 52 wt%

Figure 6. SEM micrographs of geopolymer with high content of alkali activator formed by casting method.



Figure 7. SEM micrographs of cast geopolymers with different contents of alkali activator.



Figure 8. XRD patterns of cast geopolymers with different contents of alkali activator.



Figure 9. SEM micrographs of geopolymers with low and high contents of alkali activators formed by pressing and casting methods.

3.4 Mechanisms of microstructure evolution of geopolymers

The combination of SEM, FTIR, and XRD results could propose the mechanisms of microstructure evolution for each of the two methods as shown in Figure 10. For the pressing method (Figures 10(a) to 10(c)), the semidry powders that resulted from mixing the calcined waste with the lower content of alkali activator, was compressed using a hydraulic pressing machine. After completing the mixing, the semidry powders were poured in a steel mold and the pressures were applied to eliminate large air volumes (between the powder particles) to create the compact matrix. The powders were highly compacted, and this led to the formation of geopolymerization reaction on the adjacent surface between alkali activator and wet calcined waste particles. Consequently, the surfaces of these particles in the compact metrics were dissolved by the alkali activator, thereby producing Si^{4+} and Al^{3+} ions in solution. These ions were coordinated in silicate tetrahedral ([SiO(OH)₃]⁻) and aluminate tetrahedral ([Al(OH)₄]⁻) monomers in the alkali activator. Subsequently, the monomers were incorporated by polymerization reaction into stable oligomer which was the geopolymeric gel. This paper suggests that the geopolymeric gel can fill into the pores of geopolymer specimens and lead to the occurrence of denser microstructures with the reduced pore contents.

For the casting method (Figures 10(d) to 10(f)), the geopolymer paste that resulted from mixing the calcined waste with the higher content of alkali activator, was cast in a silicone mold and then vibrated on the vibrating table. The greater number of air bubbles moved toward the surface of the geopolymer paste when the content of alkali activator was increased. After 1 day, the geopolymer samples were removed from their molds after initial hardening of geopolymer paste had occurred, and the samples were then allowed to cure for 7 days. After the geopolymerization reaction, many air bubbles or larger pores remained in the geopolymer samples because the geopolymer paste had a high viscosity and a lower workability [27,30]. Moreover, this work proposes the reason for the cracking of geopolymer samples. It is suggested that the higher alkali activator contents used for the cast geopolymers resulted in higher shrinkage and the subsequent formation of cracks because the content of alkali activator solution exceeds the requirement for the geopolymerization process may weaken the geopolymer structure. In addition, the excess content of alkali activator also resulted in the hindering process of geopolymerization and the formation of sodium carbonate, sodium hydroxide, and zeolite phases. This research believed that the larger pores, the higher cracks density and the hindering process of geopolymerization were expected to adversely impact the compressive strength of these samples.



Figure 10. Schematic mechanisms of microstructure evolution of geopolymers with low and high contents of alkali activators formed by pressing and casting methods.

3.5 Mechanical properties of geopolymers

The influence of geopolymers contained the low and high contents of alkali activators by pressing and casting on the compressive strength is shown in Figure 11. For the pressed geopolymers, the compressive strength increased with an increase in the contents of alkali activator from 20 to 24 wt% but remained constant from 24 to 26 wt%. With respect to lower alkali activator proportions, the 20 and 22 wt% alkali activator samples exhibited lower compressive strengths; i.e., 12.55 and 18.39 MPa, respectively. In contrast, sample produced with higher proportions of alkali activator (i.e., 24 and 26 wt%) obtained higher compressive strengths (i.e., 26.98 and 27.74 MPa, respectively). The compressive strength of geopolymers produced with 24 and 26 wt% alkali activators increased approximately 114.98% and 121.04% compared to those sample produced with 20 wt% alkali activators. Therefore, lower proportions of alkali activator reduce the degree of the geopolymerization reaction, which in turn reduces the compressive strength. Higher proportions of alkali activator resulted in higher compressive strengths for the pressed geopolymers because of the higher dissolution capacities for the Al³⁺ and Si⁴⁺ ions from the calcined kaolin processing waste, which increased the formation of monomers and geopolymeric gel in the geopolymerization process. Leong [10] and Duxson [31] reported that the amount of aluminosilicate gel formed was related to the compressive strength of geopolymers (i.e., increased gel formation leads to higher compressive strengths). From SEM micrographs in Figure 5, the amount of geopolymeric gel increased with increasing content of alkali activator. This gel could fill in the pores of the pressed geopolymer samples, which resulted in denser samples and higher compressive strengths. Moreover, the lower water absorptions, the slightly increased bulk densities, and the lower apparent porosities also contributed to these results.

For the cast geopolymers, the compressive strength clearly decreased when the content of alkali activator was increased. The compressive strengths of cast geopolymers produced with alkali activators of 46-52 wt% were 22.30-14.53 MPa, respectively. The lowest compressive strength of the cast geopolymer was measured for sample produced with 52 wt% alkali activator; the strength of these samples decreased approximately 53.48% in comparison to samples produced with 46 wt% alkali activator. The geopolymers prepared with lower proportions of alkali activator exhibited higher compressive strengths than the geopolymers prepared with higher content of alkali activator. This can be explained by the pores in geopolymer samples. The geopolymer prepared with the higher content of alkali activator (52 wt%) had the highest apparent porosity (Table 3) and indicated the most porous microstructure and highest crack density per the SEM image in Figure 9. Furthermore, one factor affecting the strength of the cast geopolymers was the content of alkali activator. The content of alkali activator within the samples, increased the Si⁴⁺ and Na⁺ ions available for geopolymerization, which resulted in a decrease in the compressive strength. The excessive Si⁴⁺ ion content inhibited geopolymerization due to the precipitation of aluminosilicate [12]. The excessive Na^+ ion content in the presence CO_2 in air may result in the formation of Na₂CO₃. The presence of Na₂CO₃ may decrease the compressive strength of geopolymers [32] since Na₂CO₃ reduces the degree of geopolymerization because of the high alkali concentration and due to the relatively weak binding and exchangeability of Na in the geopolymer structure [33]. FTIR spectra and SEM/EDX in this work support the formation of Na₂CO₃ in the cast geopolymer samples. Takeda et al. [34] reported that the compressive strength of geopolymer produced from metakaolin by casting was approximately 10-20 MPa after curing for 72 h at 80°C. In comparison, the compressive strength of geopolymer derived from calcined kaolin processing waste by casting and pressing this work was higher than that from metakaolin by casting in research of Takeda et al.



Figure 11. Compressive strength of geopolymers with low and high contents of alkali activators formed by pressing and casting methods.

Additionally, the compressive strengths of pressed geopolymer samples were directly compared to cast geopolymer samples. The results indicate that processing has a very important effect on the compressive strength of geopolymers. The compressive strength of the pressed geopolymer was approximately 24.39% higher than that of the cast geopolymer. This result could be explained in many ways. First, the higher compressive strength could attribute to sample compaction, fewer pores and no observable cracks (per the SEM images of the pressed geopolymers). Furthermore, the lower water absorption, the higher bulk density, and the lower apparent porosity of the pressed geopolymers, are also expected to enhance the compressive strength. In addition, FTIR and SEM analysis did not reveal the presence of Na₂CO₃ in the pressed geopolymer. This result is assumed due to the smaller proportion of alkali activator used in the pressed geopolymers compared to the cast geopolymers. In this study, it was clearly demonstrated that the pressing method resulted in higher compressive strengths in comparison to the casting method.

4. Conclusions

The mechanisms of microstructure evolution of geopolymers, the microstructure of the pressed geopolymer with lower content of alkali activator showed a dense microstructure because of higher compacted matrices (closeness of particles), resulting in the better gepolymerization reaction and the macro crack did not appear in the pressed geopolymer. The microstructure of another part, the pore formation from air bubbles, the macro cracks and the hindering process of geopolymerization were found in the cast geopolymer, in which a higher proportion of alkali activator was used. Thus, the compressive strength values obtained from the pressed geopolymers were higher than those of the cast geopolymer because the pressed geopolymer had better geopolymerization reaction, denser microstructure, no observable cracks, no Na₂CO₃, and lower porosity. The highest compressive strength values of the pressed and cast geopolymer samples were 27.74 and 22.30 MPa when the contents of alkali activators were 26 wt% and 46 wt%, respectively. The compressive strength of the pressed geopolymer was approximately 24.39% higher than the compressive strength of cast geopolymer. Therefore, from this work, the compressive strength, microstructure, and properties of geopolymers were strongly dependent on the forming process and that preparing geopolymers by the pressing method could improve the compressive strength in comparison to geopolymers prepared by the casting method. Moreover, geopolymers synthesized from calcined kaolin processing waste and lower content of alkali activator by pressing method were to solve the environment problems, reduce production cost of geopolymers, and produce geopolymer brick.

5. Acknowledgments

The authors of the present work gratefully acknowledge the financial support provided by the Royal Thai Government Science and Technology Scholarship, Thailand.

References

- [1] E. Prud'homme, P. Michaud, E. Joussein, C. Peyratout, A. Smith, and S. Rossignol, "In situ inorganic foams prepared from various clays at low temperature," *Applied Clay Science*, vol. 51, pp. 15-22, 2011.
- [2] Z. Zhang, J. L. Provis, H. Wang, F. Bullen, and A. Reid, "Quantitative kinetic and structural analysis of geopolymers. Part 2. Thermodynamics of sodium silicate activation of metakaolin," *Thermochim. Acta*, vol. 565, pp. 163-171, 2013.
- [3] R. A. A. Boca Santa, J. C. Kessler, C. Soares, and H. G. Riella, "Microstructural evaluation of initial dissolution of aluminosilicate particles and formation of geopolymer material," *Particuology*, vol. 41, pp. 101-111, 2018.
- [4] D. L. Y. Kong, J. G. Sanjayan, and K. Sagoe-Crentsil, "Factors affecting the performance of metakaolin geopolymers exposed to elevated temperatures," *Journal of Materials Science*, vol. 43, no. 3, pp. 824-831, 2008.
- [5] S. Wang, X. Ma, L. He, Z. Zhang, L. Li, and Y. Li, "High strength inorganic-organic polymer composites (IOPC) manufactured by mold pressing of geopolymers," *Construction and Building Materials*, vol. 198, pp. 501-511, 2019.
- [6] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al Bakri, M. Bnhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi and Y.M. Liew., "Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers," *Construction and Building Materials*, vol. 35, pp. 912-922, 2012.
- [7] Y. M. Liew, C. Y. Heah, A. B. Mohd Mustafa, and H. Kamarudin, "Structure and properties of clay-based geopolymer cements: A review," *Progress in Materials Science*, vol. 83, pp. 595-629, 2016.
- [8] K. Sagoe-Crentsil and L. Weng, "Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part II. High Si/Al ratio systems," *Journal of Materials Science*, vol. 42, pp. 3007-3014, 2007.
- [9] S. Samantasinghar and S. P. Singh, "Effect of synthesis parameters on compressive strength of fly ash-slag blended geopolymer," *Construction and Building Materials*, vol. 170, pp. 225-234, 2018.
- [10] H. Y. Leong, D. E. L. Ong, J. G. Sanjayan, and A. Nazari, "The effect of different Na₂O and K₂O ratios of alkali activator on compressive strength of fly ash based-geopolymer," *Construction* and Building Materials, vol. 106, pp. 500-511, 2016.
- [11] A. Gharzouni, E. Joussein, B. Samet, S. Baklouti, and S. Rossignol, "Effect of the reactivity of alkaline solution and metakaolin on geopolymer formation," *Journal of Non-Crystalline Solids*, vol. 410, pp. 127-134, 2015

- [12] B. H. Mo, H. Zhu, X. M. Cui, Y. He, and S. Y. Gong, "Effect of curing temperature on geopolymerization of metakaolin-based geopolymers," *Applied Clay Science*, vol. 99, pp. 144-148, 2014.
- [13] I. Ozer and S. Soyer-Uzun, "Relations between the structural characteristics and compressive strength in metakaolin based geopolymers with different molar Si/Al ratios," *Ceramics International*, vol. 41, pp. 10192-10198, 2015.
- [14] ASTM C109/C109M-02, "Standard test method for compressive strength of hydraulic cement mortars (Using 2-in. or [50mm] cube specimens). Annual Book of ASTM Standard," vol. 04.01, 2005.
- [15] ASTM C20-00, "Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water, Annual Book of ASTM Standard. vol. 15.01." 2005.
- [16] Y. M. Liew, H. Kamarudin, A. M. Mustafa Al Bakria, M. Bnhussain, M. Luqman, I. K. Nizar, C. M. Ruzaidi, and C. Y. Heah, "Optimization of solids-to-liquid and alkali activator ratios of calcined kaolin geopolymeric powder," *Construction and Building Materials*, vol. 37, pp. 440-451, 2012.
- [17] S. K. Amin, S. A. El-Sherbiny, A. A. M. A. El-Magd, A. Belal, and M. F. Abadir, "Fabrication of geopolymer bricks using ceramic dust waste," *Construction and Building Materials*, vol. 157, pp. 610-620, 2017.
- [18] S. Prasanphan, A. Wannagon, T. Kobayashi, and S. Jiemsirilers, "Reaction mechanisms of calcined kaolin processing waste-based geopolymers in the presence of low alkali activator solution," *Construction and Building Materials*, vol. 221, pp. 409-420, 2019.
- [19] A. Gharzouni, L. Vidal, N. Essaidi, E. Joussein, and S. Rossignol, "Recycling of geopolymer waste: Influence on geopolymer formation and mechanical properties," *Materials and Design*, vol. 94, pp. 221-229, 2016.
- [20] P. N. Lemougna, U. F. Chinje Melo, M. P. Delplancke, and H. Rahier, "Influence of the activating solution composition on the stability and thermo-mechanical properties of inorganic polymers (geopolymers) from volcanic ash," *Construction and Building Materials*, vol. 48, pp. 278-286, 2013.
- [21] P. N. Lemougna, K. tuo Wang, Q. Tang, U. C. Melo, and X. min Cui, "Recent developments on inorganic polymers synthesis and applications," *Ceramics International*, vol. 42, pp. 15142-15159, 2016.
- [22] M. Cyr and R. Pouhet, "Carbonation in the pore solution of metakaolin-based geopolymer," *Cement* and Concrete Research, vol. 88, pp. 227-235, 2016.
- [23] L. Pérez-Villarejo, E. Bonet-Martínez, D. Eliche-Quesada, P. J. Sánchez-Soto, J. M. Rincón-López, and E. Castro-Galiano, "Biomass fly ash and aluminium industry slags-based geopolymers," *Materials Letters*, vol. 229, pp. 6-12, 2018.

- [24] P. N. Lemougna, A. Nzeukou, B. Aziwo, A. B. Tchamba, Kai-tuoWang, U. Chinje Melo and Xue-min Cui. "Effect of slag on the improvement of setting time and compressive strength of low reactive volcanic ash geopolymers synthetized at room temperature," *Materials Chemistry and Physics*, vol. 239, pp. 122077, 2020.
- [25] B. Pandey, S. D. Kinrade, and L. J. J. Catalan, "Effects of carbonation on the leachability and compressive strength of cement-solidified and geopolymer-solidified synthetic metal wastes," *Journal of Environmental Management*, vol. 101, pp. 59-67, 2012.
- [26] Z. Zhang, H. Wang, Y. Zhu, A. Reid, J. L. Provis, and F. Bullen, "Using fly ash to partially substitute metakaolin in geopolymer synthesis," *Applied Clay Science*, vol. 88-89, pp. 194-201, 2014.
- [27] K. L. Lin, H. S. Shiu, J. L. Shie, T. W. Cheng, and C. L. Hwang, "Effect of composition on characteristics of thin film transistor liquid crystal display (TFT-LCD) waste glass-metakaolinbased geopolymers," *Construction and Building Materials*, vol. 36, pp. 501-507, 2012.
- [28] J. H. Kim and H. S. Lee, "Improvement of early strength of cement mortar containing granulated blast furnace slag using industrial byproducts," *Materials (Basel)*, vol. 10, pp. 1-15, 2017.
- [29] Z. Zhang, J. L. Provis, A. Reid, and H. Wang, "Fly ash-based geopolymers: The relationship between composition, pore structure and efflorescence," *Cement and Concrete Research*, vol. 64, pp. 30-41, 2014.
- [30] S. Riahi, A. Nemati, A. R. Khodabandeh, and S. Baghshahi, "The effect of mixing molar ratios and sand particles on microstructure and mechanical properties of metakaolin-based geopolymers," *Materials Chemistry and Physics*, vol. 240, pp. 122223, 2020.
- [31] P. Duxson, J. L. Provis, G. C. Lukey, S. W. Mallicoat, W. M. Kriven, and J. S. J. Van Deventer, "Understanding the relationship between geopolymer composition, microstructure and mechanical properties," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 269, pp. 47-58, 2005.
- [32] Z. Zhang, J. L. Provis, X. Ma, A. Reid, and H. Wang, "Efflorescence and subflorescence induced microstructural and mechanical evolution in fly ash-based geopolymers," *Cement and Concrete Composites*, vol. 92, pp. 165-177, 2018.
- [33] E. Najafi Kani, A. Allahverdi, and J. L. Provis, "Efflorescence control in geopolymer binders based on natural pozzolan," *Cement and Concrete Composites*, vol. 34, pp. 25-33, 2012.
- [34] H. Takeda, S. Hashimoto, H. Yokoyama, S. Honda, and Y. Iwamoto, "Characterization of zeolite in zeolite-geopolymer hybrid bulk materials derived from kaolinitic clays," *Materials (Basel)*, vol. 6, pp. 1767-1778, 2013.