Properties of hydroxyapatite based geopolymer synthesized from bituminous fly ash

S Yoolamnan1*, S Asavapisit1*, R Piyapanuwat2

1 Environment Technology Program, School of Energy, Environment and materials, King Mongkut’s University of Technology Thonburi, Bangkok, Thailand.
2 Innovative Environmental Management and Smart Construction Material Laboratory, King Mongkut’s University of Technology Thonburi (Ratchaburi Learning Park), Rang Bua, Chom Bueng, Ratchaburi, Thailand.

*Corresponding author: sirirat.95@mail.kmutt.ac.th, suwimol.asa@kmutt.ac.th

Abstract This research studied the engineering properties of hydroxyapatite based on fly ash-geopolymer as a biomaterial. The ratio of Na2O/SiO2 and K2O/SiO2 at 0.15 0.20 0.25 0.3 by mole, 2.5 5.0 7.5, 10 wt.% of calcium phosphate and heat treatment at 500°C, 600°C and 700°C for 2 hours were used to studied changed of compressive strength and crystalline phase in samples. The results observed highest 28-days compressive strength of 21.99 and 19.14 MPa for 0.20 by mole of Na2O/SiO2 and 0.15 by mole of K2O/SiO2, respectively. When calcium phosphate (CP) was added in fly ash-geopolymer, the optimum ratio of CP was found in 2.5 wt.% that have unconfined compressive strength (UCS) of 19.03 and 13.60 MPa for NaOH and KOH activator. After heat treatment of geopolymer at 500°C, the maximum compressive strength at 9.09 MPa and 22.76 MPa for each activator was obtained. Finally, the XRD resulted show hydroxyapatite, mullite quartz and sodium aluminum silicate peaks in both fly ash-geopolymer with NaOH and KOH and 2.5% CP.

1. Introduction
The development of biomaterial as bone implant must consider bioactivity and biocompatibility with bone and blood in the human body. Biomaterials which were used in human such as bio-ceramic, TiO2, composite materials. The most popular bio-ceramic material being used is hydroxyapatite (HA). It is belonging to CP compound that is quite similar to bone. Human bone consists of 60% inorganic component (or HA), 30% organic component and 10% water relative to the weight of bone [1]. HA can be synthesized using various methods, including dry, wet, thermal, and combination. Several factors affecting the synthesis of HA including pH, temperature, and the molar ratio of chemical. Generally, HA has a Ca/P ratio around 1.667 [2]. The result of each method produced a different size, morphologies, and crystalline phases of the products. Even if there are various methods to synthesise HA, the materials needed for the synthesis were too complicated [3].

Geopolymer is an aluminosilicate compound that was formed by the reactions between silica (SiO2) and alumina (Al2O3) in the presence of alkaline activators such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) [4]. Geopolymers have high strength similar to concrete but less CO2 emission in production process. Mackenzie et al. [5] and Herve et al. [6] synthesized geopolymer and use as
supporting material for the formation of HA. The geopolymer cement with HA has the compressive strength greater than 40 MPa that can be used as a bone implant. Therefore, the aim of this research was to synthesize HA-based geopolymer from bituminous fly ash. The performance of HA-based geopolymer was assessed through the development of UCS and microstructures.

2. Experimental

2.1. Materials and Chemicals

The fly ash (FA) was used for the synthesis of geopolymer. FA from BLPC power company in Rayong province, Thailand has chemical compositions as determined by XRF is shown in Table 1. SiO$_2$, Al$_2$O$_3$, CaO, and Fe$_2$O$_3$ were the major elemental oxide contents of FA and were present at 53.6, 25.4, 8.25, and 5.89%, respectively. XRD result in Figure 1 shows the appearance of the crystalline phases of quartz and mullite with the presence of amorphous phase between 18 and 28 degrees of 2 theta. Commercial grade chemicals in this research including NaOH from Formosoda-p, Taiwan, KOH from UNID, Korea and CP from FDSCL, Mumbai having purity of 99, 95 and 99%, respectively were used.

| Chemical composition | SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | TiO$_2$ | SiO$_2$/Al$_2$O$_3$ |
|----------------------|--------|------------|-----|------------|--------|-------------------|
| % by weight of FA     | 53.6   | 25.4       | 8.25| 5.89       | 1.63   | 2.1               |

Figure 1. XRD diffractogram of FA

2.2. Preparation and testing

2.2.1. Preparation HA-geopolymer paste

The geopolymer was synthesized from FA and alkaline activators (NaOH or KOH) with a ratio of Na$_2$O/SiO$_2$ and K$_2$O/SiO$_2$ of 0.15, 0.2, 0.25, and 0.3 by mole. All materials were mixed with a mechanical mixer, following ASTM D1633-17. The mixtures were placed in cylindrical polyvinylchloride (PVC) molds with a 35 mm diameter and a 70 mm height. All samples were demolded after 24 h curing, stored at room temperature and kept for 7, 14, and 28 days prior the strength measurement. The proportion having maximum UCS was selected for the addition of 2.5, 5, 7.5, and 10 wt.% of CP and following heat treatment at 500, 600, and 700°C for 2 h.

2.2.2. Method for testing

The mechanical property of all samples was measured by compaction following ASTM D1633-07 [7]. Each mix proportion was prepared for 6 replications and to be used for UCS determination. Strength
results were presented with 95% confident level. In addition, the selected proportions of the cracked samples from UCS testing were kept for microstructural study by XRD technique.

3. Results and discussion

3.1 Effect of the alkaline activators on compressive strength of FA-based geopolymer.

The UCS of FA-based geopolymer as a function of increasing alkaline concentration and curing time are shown in Figure 2 (a, b). UCS increased with increasing curing time at all concentrations of both alkali activators. The highest UCS at the age of 28 days was obtained from samples with 0.2 Na$_2$O/SiO$_2$ and 0.15 K$_2$O/SiO$_2$ having strength of 21.99 and 19.14 MPa, respectively. The highly alkaline of both activators (NaOH or KOH) dissolved silica (SiO$_2$) and alumina (Al$_2$O$_3$) from the surface of FA particles. The soluble silica and alumina species then react with Na$^+$ or K$^+$ cations from alkali activators and transform into a tetrahedral framework of sodium or potassium aluminosilicate [8,9]. This resulting in the development of strength of the FA-based geopolymer.

![Figure 2. UCS of FA-based geopolymer with activators of (a) NaOH and (b) KOH](image)

At lower alkali concentration than the optimum value, lower amounts of silica and alumina were dissolved from FA. Therefore, lower geopolymer products are formed and leading to lower strength. On the other hand, at higher alkaline concentration of both alkali activators than the optimum value, lower strength of geopolymers were gained (Figure 2 and 3). This phenomenon was caused by the highly alkaline environment of high concentration activators accelerates the dissolution of silica and alumina from FA. Another explanation could be caused by a higher viscosity and temperature of the mixtures with high concentration of alkali activators leading to a rapid precipitation of geopolymer on the surface of FA particles. This could obstruct the geopolymerization reaction and thus lower strength was observed [8]. From this experiment, the optimum concentrations of NaOH and KOH at 0.2 Na$_2$O/SiO$_2$ and 0.15 K$_2$O/SiO$_2$ were selected for further study.

3.2 Effect of Calcium phosphate on compressive strength of HA-based geopolymer

A 28-days strength of FA-based geopolymer activated with NaOH varied from 21.99 MPa with no addition of CP to 19.03, 17.92 and 17.78 MPa with the addition of 2.5, 5.0 and 7.5 wt.% of CP, respectively (Figure 3 (a)). Similar variations of strength were obtained for FA-based geopolymer activated with KOH but lower strength was gained (19.14 MPa with no addition of CP to 13.60, 14.01 and 14.00 MPa with the addition of 2.5, 5.0 and 7.5 wt.% of CP, respectively) as is shown in Figure 3(b). Addition of CP causes an imbalance of ionic species in the mixtures due to Ca$^{2+}$ and PO$_4^{3-}$ which interfering the normal geopolymerization reactions resulting in less formation of geopolymer products thus leading to lower strength of FA-based geopolymer [6]. From the experimental results, the
concentration of 2.5 wt.% CP was selected for FA-based geopolymer activated with both NaOH and KOH to study the heat treatment on strength of HA-based geopolymer.

Figure 3. UCS of FA-based geopolymer activated with activators of (a) NaOH or (b) KOH and (c) NaOH or (d) KOH at various amounts of Ca$_3$(PO$_4$)$_2$

3.3 Effect of temperatures on compressive strength of HA-based geopolymer

Figure 4 shows a strength of HA-based geopolymer with both activations and 2.5 wt.% of Ca$_3$(PO$_4$)$_2$ addition after treatment at 500-700°C gain strength of 9.09, 7.37 and 5.74 MPa for samples with NaOH and 22.76, 15.82 and 20.18 MPa for samples with KOH, respectively. The highest strength was obtained from samples treated at 500°C. A continue reduction of strength for samples activated with KOH was observed after treatment at the temperature at 600°C and 700°C. This could be caused by the presence of an increase micro-cracking with increasing treatment temperature [5, 10, 11].

Figure 4. UCS of HA-based geopolymer after treatment at 500, 600 and 700°C

3.4 XRD results

Figures 5. a-d show XRD patterns of HA-based geopolymer activated with 0.2 of Na$_2$O/SiO$_2$ or 0.15 of K$_2$O/SiO$_2$ in the presence of 2.5% of calcium phosphate. XRD diffractograms reveals the presence of the crystalline phases including HA, mullite and quartz in all samples except for the samples activated with NaOH also found sodium aluminum silicate and KOH found potassium aluminum silicate. This is in agreement with the previous research [5,6].
4. Conclusions
From the strength results, the optimum alkali activator, CP, and temperature of heat treatment for the synthesis of HA-based geopolymer from FA were 0.2 mole of Na$_2$O/SiO$_2$ or 0.15 mole of K$_2$O/SiO$_2$ with the addition of 2.5 wt.% of CP and treatment at temperature of 500°C. XRD results reveals the appearance of crystalline phase of HA from samples with and without heat treatment. Leachability of Al, Si, Ca, and P from the HA-based geopolymer samples will be investigated for the future work.

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Figure 5. XRD diffractograms of (a) HA-based geopolymer with NaOH, (b) HA-based geopolymer with NaOH and treated at 500°C, (c) HA-based geopolymer with KOH and (d) HA-based geopolymer with KOH treated at 500°C

M: mullite,
Q: quartz,
H: hydroxyapatite,
N: sodium aluminum silicate,
K: potassium aluminum silicate