On Valorization of Volcanic Ash, Waste Pen Shells, and Red Clay to Synthesize Geopolymers

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Abstract

This study utilizes volcanic ash and red clay, as well as calcined waste pen shell (Baluko) in the production of geopolymer-based materials. The geopolymers were formed by activating the mixture of these raw materials (as the alumina-silica rich materials) with activating solution of a 12M NaOH/Na2SiO3 (w/w: 2.5:1). Two sample types, a cube type and a slab type, were used in the study in order to conform to test standards for compressive strength and fire resistance test. The cube type molds were for the compressive strength tests while the slab type is used for the fire resistance tests. Material testing such as Fourier Transform Infrared (FTIR) were also used to analyze the chemical characteristics of both the raw materials and the geopolymer specimens. The mixture containing 45% Volcanic Ash-45% Red Clay-10% waste shell was observed to have the highest compressive strength out of all the samples. The fire resistance of the geopolymers formed from a ternary mixture of 16% Volcanic Ash-66.67% Red Clay- 16% waste shell powder was also observed to be comparable to that of Ordinary Portland Cement. Furthermore, the FTIR results of both raw materials and geopolymer showed evidence that geopolymerization occurred in the samples, indicating that the selected precursors are viable for use in the formation of geopolymers.

Keywords: Geopolymer, volcanic ash, red clay, waste penshell

Introduction

Geopolymer is a kind of aluminosilicate polymer which is dubbed as a next-generation cement but with a lower carbon footprint and embodied energy as compared to Portland cement [1-3]. Some of its properties are high compressive strength, good chemical resistance and high temperature resistance are attibuted to its three-dimensional structure of aluminate and silicate tetrahedra joined by oxygen corners [4, 5]. Some recent study shows that geopolymer could also be utilized for wastewater treatment, heavy metal adsorbent, and as a heterogeneous catalyst [6-9].

Geopolymer technology allows for waste valorization such that waste materials like coal ash, rice hull ash, red mud waste and natural minerals from volcanic ash can be used as an aluminosilicate raw materials. These so-called potential geopolymer precursor when reacted with activating solution forms such cementitious material [10-12]. This study thus explores the locally available materials such as volcanic ash, waste pen shells, and red clay from the Philippines to form geopolymer-based materials. Red clay is a naturally occurring soil that are rich in iron-containing minerals and can be found in some regions in the Philippines. As the country has numerous volcanoes, it is also not surprising to have an abundant source of volcanic ash which is a mixture of particulates such as crushed rocks, minerals and glass expelled from eruptions. On the other hand, waste pen shells are waste generated from the locally known as "*Baluko*" shell, which is very abundant in some parts of Philippines such as Sorsogon in Bicol region. Note that these scallops of the "*Baluko*" are cooked and served as a local delicacy. The waste shells are commonly used as decorative material while majority of it has gone as waste in the landfill or in the ocean. This shell is a good source of calcium and the calcined shell could be utilized to make a composite geopolymer with fly ash [13]. Use of such indigenous resources and waste as raw materials for geopolymer precursor mitigates not only the waste's environmental footprint but also contributes towards a circular economy in producing eco-friendly materials.

Materials and Method

Preparation of Raw materials

Three local materials namely volcanic ash, red clay and Baluko shells were sourced out from Bicol region in the Philippines as shown in Figure 1. Since the materials like volcanic ash and red clay are damp, rocky, and clumped together, drying and grinding to powder was necessary to achieve a particle size of not greater than 150 micrometers. As for the Baluko (waste pen) shells, these had to be washed first with sodium hypochlorite to remove contaminants that cling onto the shell before oven drying at 110 degrees. The dried shells (BS) were then calcined at 700 ºC in a muffle furnace. The raw materials are then characterized using Fourier Transform Infrared (FTIR).

Figure 1. Raew materials namely a) volcanic ash, b) red clay c) baluko shells

Synthesis and evaluation of geopolymer

The activating solution was prepared by mixing 12M sodium hydroxide (NaOH) solution with water glass solution in a ratio of 2.5 : 1. The solid to liquid ratio of 0.25 by mass was maintained in all mixtures. In every mixture, a total of 2.8 kilograms of dry material was used to produce 15 cubes. Following the mix design described in Table 1, 2.8 kilograms of dry material was portioned among the 3 raw materials. The fresh mix is then placed in the appropriate mold wherein the curing period for both the type 1(cube) and type 2(slab) samples is 28 days. Two pre-curing conditions for one day were also done namely the ambient temperature and the other set is at 80ºC in an oven. Compressive strength was measured using the Universal Testing Machine (UTM) whereas ASTM E119: Standard Test Methods for Fire Tests of Building Construction and Materials (Standard Fire Test) were used for fire resistance test. Fourier Transform Infrared (FTIR) analysis was also conducted to the geopolymer specimens.

Table 1. Mix Proportions of the specimens

Mixture Code	Volcanic Ash, VA (%)	Red Clay, RC (%)	Waste pen (Baluko) Seashell, BS (%)
UCL008	75	25	0
UCL009	50	50	0
UCL010	45	45	10
UCL011	66.67	16.67	16.67
UCL012	16.67	66.67	16.67
UCL013	75	0	25
UCL14	25	75	0
UCL015	0	75	25

Results and Discussion

Figure 2 shows the infrared spectrum of the uncalcined red clay. The values indicated in the waveforms are the peaks in which there are bonds and minerals essential in geopolymerization. The peaks from 3693.39-3623.85 cm^{-1}indicate that Kaolinite is present. Kaolinite is a major constituent of red clay which gives sharp absorption bands in the 3700-3600 cm^{-1}region [14]. The band at 1040 $cm^{-1}$is due to asymmetric stretching vibrations of silicate tetrahedron [14]. The peak at 792.65 indicates the presence of quartz which is explained by the Si-O stretching vibration. On the other hand, the peak at 676.98 cm^{-1}indicates a Si-O symmetric bending vibration due to low level of Al for Si substitution. The band at 538.35 $cm^{-1}$is due to the presence of hematite. It overlaps into one broad adsorption band centered at 535 cm^{-1}assignable to Fe-O present in kaolinite [14]. The region between 3000-2850 cm^{-1}indicates that there is a presence of organic matter. More specifically, the peaks at 2927.3 and 2860 cm^{-1} correspond to the C-H stretching vibrations of some organic contribution [15].

Figure 3 shows the Infrared Spectrum of the Uncalcined Baluko Shell and Calcined Baluko Shell. For the Uncalcined Baluko Shell, a broad absorption around 3421.55 $cm^{-1}$is caused by the O-H stretching vibration. The peak at 3642.18 cm^{-1} indicates a sharp O-H stretching band upon calcination. The peak at 1453.6 cm^{-1} indicates a bending vibration of the O-Ca-O functional group. The Baluko shells, being primarily composed of calcium carbonates, only act as aggregates and do not fully contribute to the geopolymerization process. On the other hand, FTIR pattern from the calcination process indicate a new peak which appears at 3,620 cm^{-1}; this evidence indicates the formation of basic OH groups which attached to the calcium atoms, which could make the calcined clay more reactive to form cementitious-like structure.

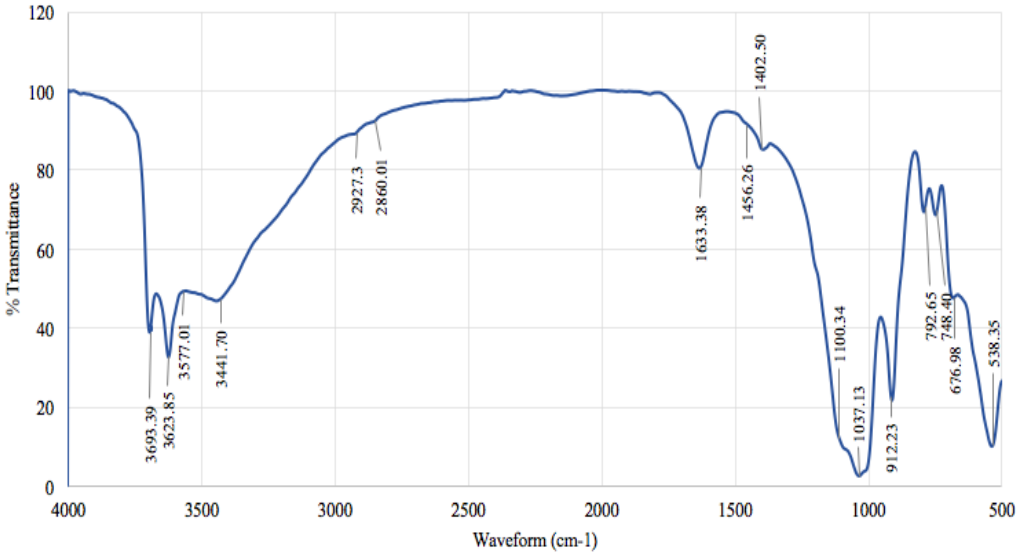

Figure 2. FTIR pattern of uncalcined red clay

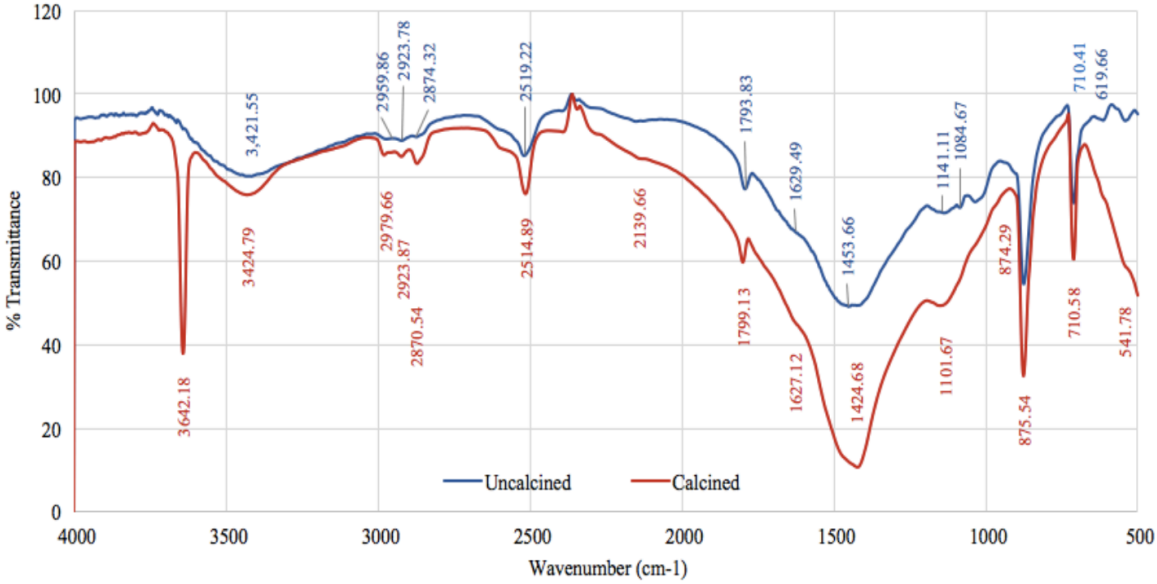

Figure 3. FTIR pattern of uncalcined and calcined Baluko shell

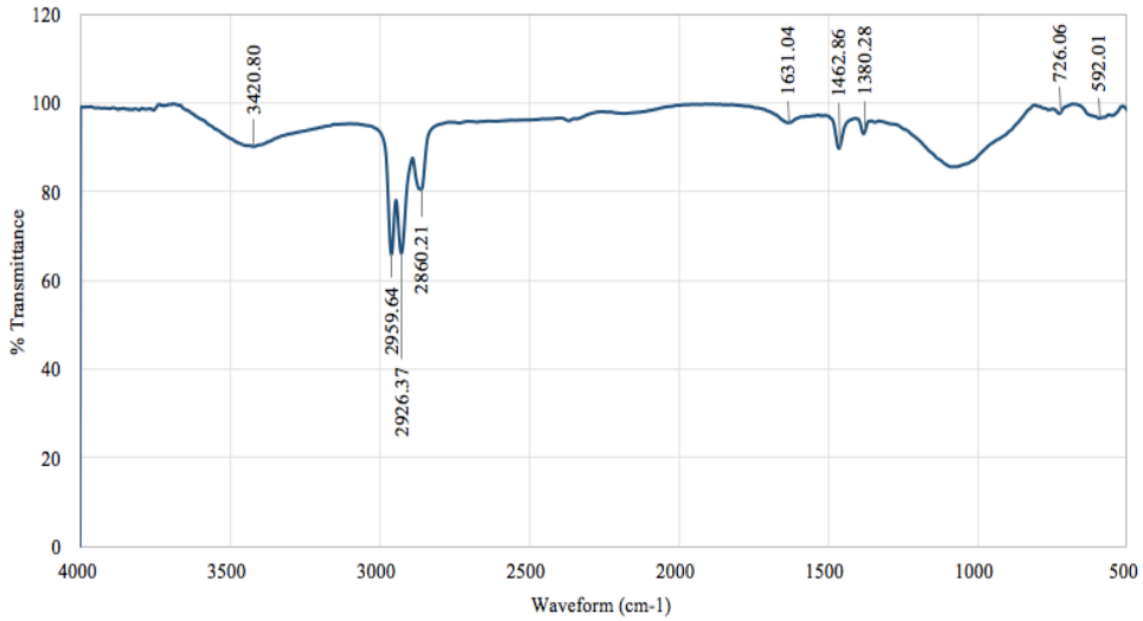

Figure 4. FTIR pattern of volcanic ash

Figure 4 shows the infrared spectrum of the uncalcined volcanic ash. The bands at 726.06 cm^{-1} and 592.01 cm^{-1} indicate ring vibrations of Si-O bonds of the silicate network. The main band related to the vibration of SiO/Al-O bond of aluminosilicate framework is located at 1014 cm^{-1}. The peaks that were observed at 3420.80 cm^{-1} and 1631.04 cm^{-1} indicate that there is a stretching and bending vibration of O-H bonds from silanol group and water molecules. The peaks at 2926.37 cm^{-1} and 2860.21 cm^{-1} may relate to C-H vibrations bond of methane [16]. Fig.4 also shows that the bands at 757, 580, and 545 cm-1 are related to the ring vibrations of Si–O bonds of silicate network. The peak observed at 472 cm-1 corresponds to the vibration of Si–O–Fe bond. The main band related to the vibration of SiO/Al–O bond of aluminosilicate framework is located at around 1014 cm-1. The bands observed at 3420 and 1630 cm^{-1} are characteristic of stretching and bending vibrations, respectively, of O–H bonds from silanol group and water molecules. The bands at 2917–2856 cm^{-1} might correspond to C–H vibration bonds of methane dissolved into glassy phase. The absorption bands at 2366 and 1754 cm^{-1} indicate the presence of carbonates which are physically adsorbed to glassy phase in the form of CO_2 molecule. The presence of water, methane, and CO_2 is very common in aluminosilicate glasses [16].

Figure 5 shows spectra of some of the geopolymer specimens produced from this experiment. The peak at around 1600-1630 indicate a H-OH bending vibration and is typical for polymeric structures including aluminosilicate. At around 1400, O-C-O stretching of carbonates occur. The peaks ranging from 1200-950 indicate that there is a T-O-Si asymmetric stretching, in which T can either be Al or Si. The key feature of the spectra are the bands around 1000 cm^{-1} to 900 cm^{-1} which indicates the presence of geopolymeric structutre.

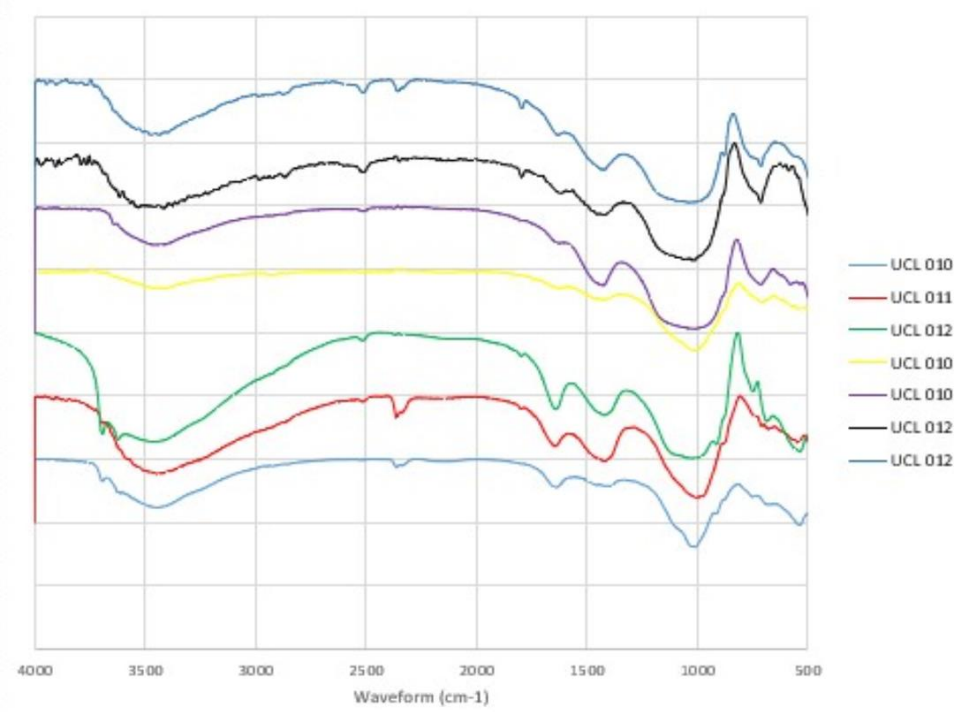

Figure 6. FTIR pattern of geopolymer specimens

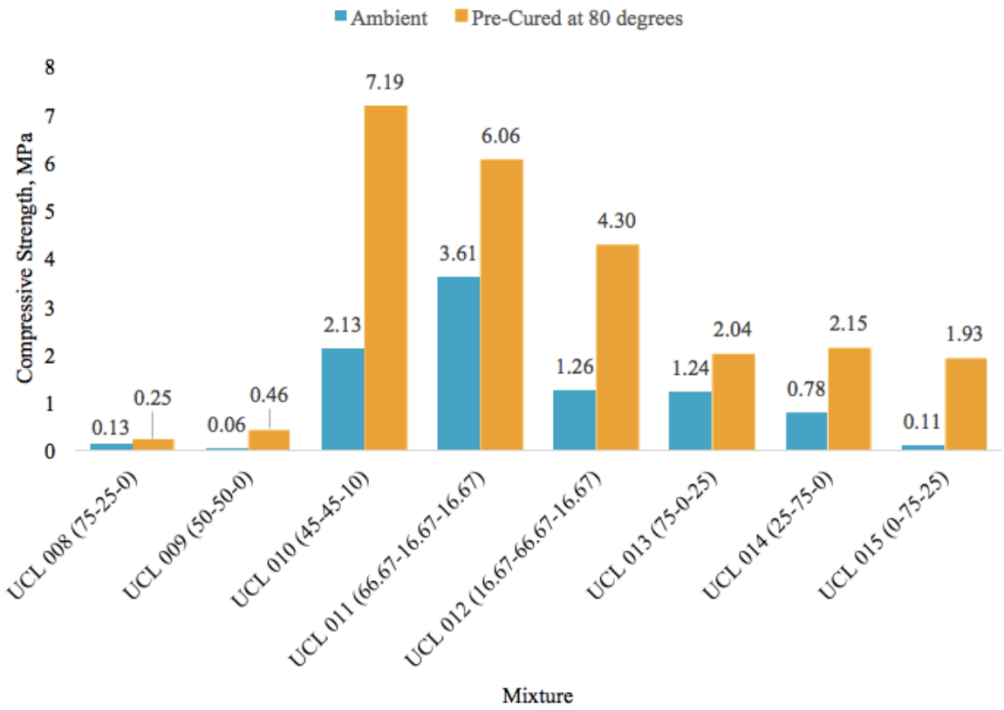

Figure 7. Compressive strength of geopolymer specimens

As shown in Figure 7, the mean compressive strengths of the produced geopolymer binders vary over a range of 0.06MPa or 60 KPa to 3.61MPa or 3,610 KPa for the samples cured at ambient conditions, whereas the mean compressive strengths of the pre-cured samples varies over a range of 0.25MPa to 7.19MPa. These results indicate that the pre-curing of the samples at an elevated temperature has resulted in an overall gain in the mean compressive

strength of the geopolymer binders, achieving a 161.72% increase. The increase in compressive strength could be due to the elevated pre-curing temperature assisting in the formation of geopolymer bonds in the samples [10], as well as the removal of excess moisture content from the geopolymer binder which was found to be a characteristic common to all geopolymer binders containing red clay as a raw material.

Moreover, the samples formed from ternary mixtures of volcanic ash, red clay, and calcined baluko seashell were observed to have higher mean compressive strengths when compared to the samples formed from binary mixtures. It can be observed that the mean compressive strength of the ternary geopolymer binder mixtures ranges from 4.3MPa to 7.19MPa, attaining the highest recorded value when equal parts of volcanic ash content (45%) and red clay (45%) content are incorporated into the mixture, with an amount of calcined baluko seashell not exceeding 10% of the whole mixture.

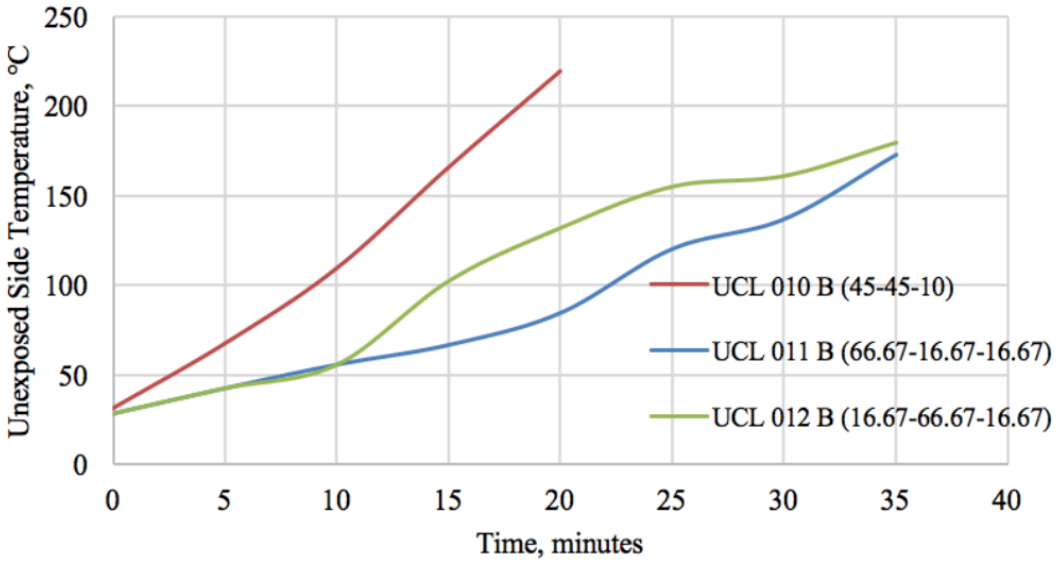

Figure 8. Fire resistance test of selected geopolymer specimens

As for the fire resistance as shown in Figure 8, UCL 010 showed the fastest increase in temperature, hence reaching its failure temperature within 17 minutes of direct fire exposure followed by UCL 012 which reached its failure temperature within 28 minutes of exposure. These mixtures in fact, contained the greatest volcanic ash contents. This proves that volcanic ash does not contribute greatly to the fire resistance of the resulting geopolymer binder. On the other hand, UCL 011 and UCL 012, being the mixtures that withstood the fire resistance test the longest, contained equal amounts of Baluko. Hence, there is a positive correlation between the fire resistant properties of the material and the amount of calcined Baluko shells present in the mixture. Previous studies in our laboratory suggest comparable fire resistance performance with Ordinary Portland Cement (OPC) material.

Conclusions

Volcanic ash, red clay and waste "*Baluko*" shell were valorized to produce geopolymer-based materials. A mix proportioning which contains 45% Volcanic Ash- 45% Red Clay-10% calcined waste shell was observed to have the highest compressive strength out of all the samples. The fire resistance of the geopolymers formed from a ternary mixture of 16% Volcanic Ash-66.67% Red Clay- 16% calcined waste shell powder was observed to be comparable to that of OPC. Furthermore, the FTIR results showed evidence that geopolymerization occurred from the activation of these raw materials indicating that the selected precursors are viable for use in the formation of geopolymers. Thus, future work will investigate further the optimization of the properties of the geopolymer product.

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