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Utilization of Waste Coal Fly Ash and Baluko Shells as Precursors for Geopolymer Beads

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Abstract: The superior mechanical properties and resistance to chemical attacks of geopolymers are well established. This material is typically formed by treating waste materials such as coal fly ash (a by-product of coal combustion), metakaolin, and calcined waste seashells with an alkali activator. For these reasons, plenty of research today focuses on their use as alternatives to conventional cements. However, recent developments have started investigating their potential as carriers for active nanomaterials, particularly when formed into spherical or bead-like shapes with increased porosity. With waste utilization and product improvement in mind, this study focuses on developing geopolymer beads from fly ash and waste shells from the local Baluko – two materials produced in great quantities with limited industrial use. Upon application of a water absorption technique, it was found that the beads had high open porosity at an average of 46.36%.

Key Words: geopolymer; fly ash; waste pen shells; suspension solidification; nanomaterial carrier

1. INTRODUCTION

Geopolymers are an emerging class of material with promising mechanical properties and resistance to chemical attack. Their mechanical properties are akin to that of Ordinary Portland Cement (OPC); however, the process of producing geopolymers is much less energy intensive and generates less greenhouse gases. Geopolymers may also be formed by treating aluminosilicate-containing raw materials with an alkali activator. Commonly used raw materials include coal fly ash, metakaolin, and calcined waste seashells – all of which are either found in great abundance or are essentially waste materials. With these ideas in mind, geopolymers may be viewed as a more environmentally-friendly alternative to OPC (Palomo, Grutzek, and Blanco, 1999).

More recently, geopolymer spheres or beads have been gaining attention as well. These beads are roughly 3 to 5 mm in diameter and are made to have increased open porosity. They are made by mixing together the raw materials and the alkali activator to form a paste, then dropping the paste into a hot, viscous solution of a similar density (commonly PEG-600, ρ=1.12 g/mL). Because of the surface tension interactions, the paste then forms into spherical or bead-like shapes; the high temperature of the solution also ensures the rapid solidification of the bead into its final form (Tang et al, 2015; Ge et al 2015).

The geopolymer beads are meant to act as inert carriers for active compounds such as nanosilver or nanotitania. Their size, shape, and porosity give them a higher surface area to volume ratio, and thus enhanced contact with the surrounding media. Decorating the beads with either nanosilver or nanotitania imparts them with antimicrobial or photocatalytic properties, respectively. The decorated beads may then be used to treat contaminated water, and the spherical shape allows easier handling.

This study looks into developing geopolymer beads from coal fly ash and calcined waste shells of the pen shells (*Pinnidae* family), known locally as Baluko – a mollusk native to the beaches of Bicol, Philippines. According to literature, addition of calcined shells provides a source of CaO to the geopolymer, which then hastens the setting time (Djobo et al, 2016). The shorter setting time allows the beads to form and solidify faster, reducing the time required to produce the beads. Other possible sources of CaO include granulated blast furnace slag, hydrated lime, (Davis, Montes, and Arroyo, 2015), wollastonite, and calcite (Yip and van Deventer, 2002), among others. However, this study focused on using the waste Baluko shells in an effort to alleviate the waste problem in the said area.

2. METHODOLOGY

2.1 Pre-treatment of Raw Materials

First, waste Baluko shells were obtained from Sorsogon, Bicol. They were then soaked in water and bleach for a few days, and then scrubbed to remove organic matter. The clean shells were then crushed into 3 to-4 cm pieces, calcined at 700 ^{o}C for 2 hours, then sieved to mesh # 200 (75 microns).

2.2 Producing the Geopolymer Beads

The geopolymer beads were formed via suspension solidification – as previously demonstrated by Tang et al (2015). It starts with mixing together the fly ash (FA) and calcined baluko shells (BS), water, and the alkali activator for 2 minutes. A 1.5% sodium dodecyl sulfate solution (SDS) and 50% H_2O_2 solution were also added separately, with 2 minutes of mixing in between. Table 1 below shows a summary of the raw materials used, their respective amounts, and purpose.

Table 1. Mix Proportion of the Geopolymer

Component	Amount	Purpose
FA	74.67 g	Aluminosilicate source
BS	18.67 g	
NaOH	7.47 g	Alkali activator
WGS	29.87 g	
1.5% SDS	4.57 g	Increases porosity
H_2O_2	0.46 g	
H_2O	2 mL	Controls viscosity

The resulting paste was then transferred to a plunger-less syringe, then allowed to flow dropwise into PEG-600 in a water bath at 90^{o}C. The beads formed were left to fully solidify in solution for 20 minutes. After, the beads were collected, rinsed thoroughly to remove excess PEG-600, then allowed to dry and cure in an oven at 90^{o}C for 24 hours. Figure 1 shows a schematic diagram of the entire process.

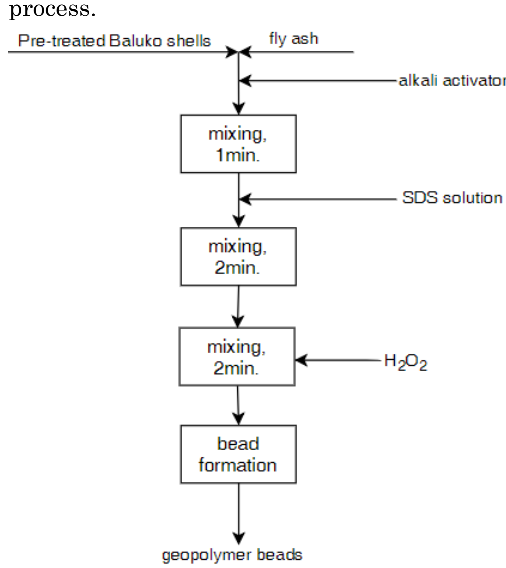

Fig. 1. Schematic Diagram

3. RESULTS AND DISCUSSION

Figure 2 shows the geopolymer beads formed. They are about 4-5 mm in diameter and the surface is visibly porous. Upon applying a water absorption technique, where the dry, suspended, and saturated weights of the beads in water are recorded, it was found that they had an average open porosity of 46.36%. This high open porosity is desirable for this experiment – this allows more of the nanoparticles to be accommodated on the surface of the geopolymer bead, creating a more potent product. Equation 1 was used to derive this value.

Fig. 2. Geopolymer Beads

$$open\ porosity = \frac{sat'd\ weight - dry\ weight}{sat'd\ weight - susp.\ weight} \qquad \text{(Eq. 1)}$$

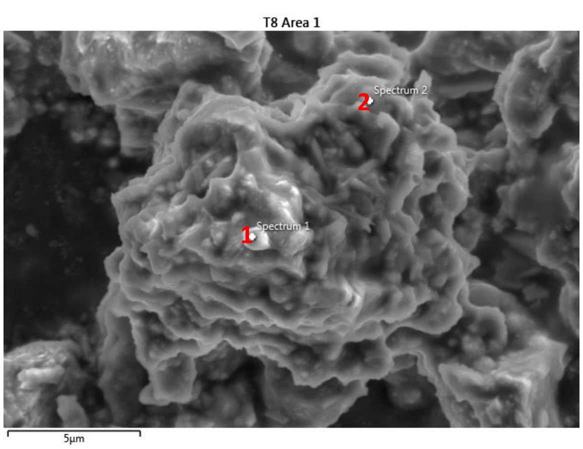

Fig. 3. SEM Image of the Geopolymer

Table 2. Elemental Analysis of the Geopolymer

	Spectrum 1	Spectrum 2
Element	Weight %	
O	33.4	42.7
Fe	28.3	6.9
C	14.5	19.2
Mg	8.9	1.7
Si	5.3	15.2
Al	5.4	8.8
Na	2.2	2.8
Ca	2.1	1.4

Figure 3 shows an SEM image of the geopolymer at 10,000x magnification. A uniform microstructure is evident from the image.

On the other hand, Table 2 shows the elemental analysis of two points on the geopolymer. Substantial amounts of oxygen atoms were found; these are attributed to the structure of the geopolymer itself, of which the oxygen atoms acts as links to the silicate and aluminate species. On the other hand, the Fe, Mg, Si, and Al and Na are attributed to the fly ash and alkali activator, respectively. Significant amounts of C are also found; this is atypical of geopolymers, which are inorganic in nature. Carbon may have been formed when CO_2 from the atmosphere diffuses into the pores – the CO_2 dissolves into the pore water to form H_2CO_3, which then attacks the Ca or Na bearing phases in the geopolymer to form $CaCO_3$ or Na_2CO_3 (Bernal et al 2010).

4. CONCLUSIONS

Geopolymer beads were successfully produced via suspension solidification using coal fly ash and calcined Baluko shells as raw materials. The beads are visibly porous and are stable even when soaked in water for hours at a time. Because of possible carbonation, small amounts of carbonates may have formed on the surface of the geopolymer.

More experiments will be conducted in the future to determine how the presence of carbonates affects the performance of the nanotitania/nanosilver-coated final product. The parameters during bead formation – such as the fly ash to Baluko shell ratio, the solid to liquid ratio, the H_2O_2 dosage, and others – will also be optimized to produce geopolymer beads with maximized open porosity and uncompromised stability in water.

5. ACKNOWLEDGMENTS

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