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MACRO- AND MICROSTRUCTURAL ANALYSIS OF BIOMASS-FIBRE REINFORCED FLY ASH GEOPOLYMER

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Abstract

The use of various types of fibres to increase the flexural strength of geopolymers is an established method. These studies focus on the use of both organic and inorganic fibre materials (e.g. steel, PP, PE etc.). However, the application of biomass fibres for the production of reinforced geopolymers is a less investigated topic in the spite of the good heat insulating properties of biomass and the high fire resistance of geopolymer.

Lignite type fly ash was used for geopolymer production with crushed woody biomass as fibre reinforcement. Fly ash was mixed with biomass fibres in 30 wt.%, 50 wt.% and 70 wt.% and geopolymer-biomass composite specimens were prepared.

The FT-IR and SEM analysis of the biomass-fibre reinforced geopolymer composites were carried out to examine the compatibility of the materials. According to the results of the micro- and macrostructural analyses, the wood particles and the geopolymer matrix showed good adhesion, with decreased amount of unreacted fly ash particles as the fibre quantity was increased. The obtained results serve as a valuable basis for further systematic investigation, as well as for additional mechanical and flexural performance tests.

Introduction

Geopolymers are synthetic alumino-silicates that can be produced from solid alumina and silica bearing materials using alkaline activator solution. The resulting products are fire and acid resistant, have good mechanical properties, low shrinkage and thermal conductivity etc. [1, 2].

Compared to ordinary Portland cement and OPC-based concrete, the production of geopolymer cement and concrete is cheaper and both are considered greener materials: these are more energy-efficient, have decreased total CO₂ emission and industrial wastes and by-products can be used as base materials (e.g. fly ash, blast furnace slag, red mud) [3, 4].

Fly ash is a by-product of coal burning and it is collected from coal fired power plants with electric or mechanical dust collectors. There are numerous applications of both raw and ground fly ash beside geopolymer production, such as cement substitute in OPC, soil fertiliser or backfilling material for abandoned mines [5, 6, 7, 8].

To improve the brittleness of the geopolymer, the development of geopolymer-fibre composites has been a focus of attention. Thus, the advantage of using fibre reinforcement in geopolymers include not only increased material greenness but the ductility of geopolymers can also be improved (Figure 11), along with the fire resistance of the fibres [9, 10, 11].

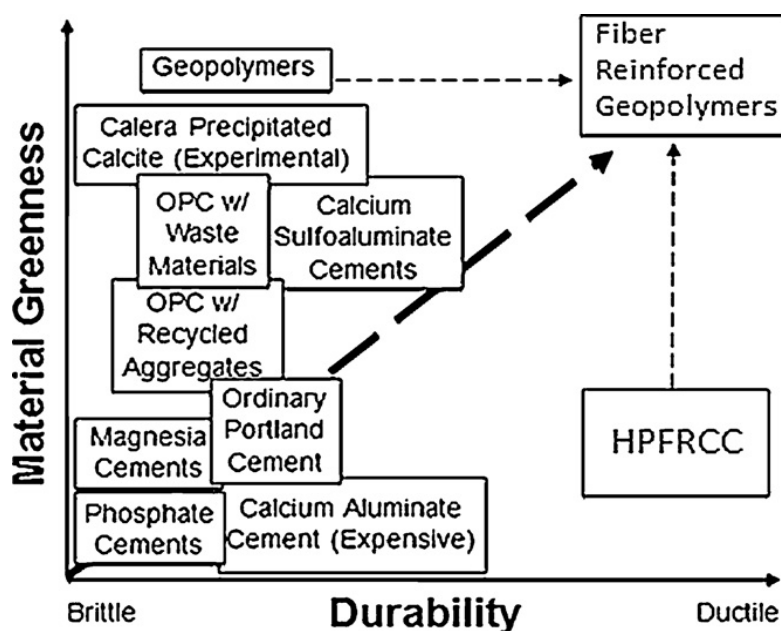


Figure 1. Fibre reinforced geopolymers in relation to material greenness and durability [9].

According to Guo and Pan [12], two types of fibres can be distinguished:

- Low modulus, high elongation fibres (nylon, polypropylene, polyethylene etc.): enhance the energy absorption characteristics.
- High strength, high modulus fibres (steel, glass etc.): enhance the strength and toughness.

The compatibility of various types of fibres with geopolymers has been examined during the last decade, some of which are summarised in Table 1.

Table 1. Fibre reinforced geopolymers in the literature

Reference	Fibre(s) used	Fibre quantity
[10]	synthetic (polyolefin), steel	8 kg/m ³ , 40 kg/m ³
[12]	polypropylene, basalt, steel	-
[13]	steel, polypropylene	1 and 2 wt.%, 0.5 and 1 wt.%
[14]	steel, polypropylene	0.5% vol fraction
[15]	steel, polypropylene	0.2-2 vol.%
[16]	polyolefin, basalt, polyamide, PVA	0.4%, 0.8% and 1.2%
[17]	steel, glass, PVA	-
[18]	steel (from waste tires)	1, 3, 5 wt.%
[19]	glass fibre waste	0-3 wt.%
[20]	waste textile cord	5%, 10%, 20%, 30% by vol
[21]	cotton	0, 0.3, 0.5, 0.7 and 1 wt.%
[22]	cotton	0.3, 0.5, 0.7 and 1 wt.%
[23]	cellulose, hemicellulose, lignin	5, 10 and 20 wt.%

Reference	Fibre(s) used	Fibre quantity
[24]	cotton, sisal, raffia, coconut	1 wt.%
[25]	PVA, starch (amylum), chitosan, gelatine, PVP, PEG, gum Arabic	5%, 10%, 15%
[26]	flax tow, flax hurds	1 wt.%
[27]	flax	1 wt.%
[28]	sawdust	0-20% with an interval of 5%

Data on geopolymers reinforced with both synthetic and natural fibres can be found in the literature. In case of natural fibres, the use of cotton fibres was extensively analysed by Alomayri et al., who found that over 5 wt.% of fibres had a negative effect on the mechanical characteristics due to increased porosity and fibre agglomeration [21, 22]. Fibres from various plants were added to geopolymer mixtures by Korniejenko et al. According to their results, natural fibres were less coherent with the geopolymer binder than synthetic fibres. In most cases, increasing the amount of fibres over an optimum level had negative effect on the mechanical properties of the composites [24, 25, 26].

The aim of the experiments was to examine the compatibility of woody biomass with the geopolymer matrix prepared with the use of lignite fly.

Experimental

For the experiments, fresh raw lignite type fly ash from Mátra Power Plant was used. The fly ash was dried until constant mass was reached and used after it cooled down.

The woody biomass used for the experiments was collected in the Botanical Garden of the University of Sopron in 2018. The estimated age of the linden tree was between 45-60 years, and the logs' diameter was 30-40 cm. After separating the cork and phloem from the wood, the fibre production was completed with a hammer mill (Figure 22) with a screen size of 10 mm.



Figure 2. The hammer mill used for fibre production

The particle size distribution of fly ash was examined with a Horiba LA950 V2 type laser particle size analyser. The geometric specific surface area (SSA) was calculated from the distribution, using shape factor 1.75.

The composition of the geopolymer activator solution was 75 wt.% water glass and 25 wt.% 8M NaOH solution. In the geopolymer-biomass composites, 30 wt.%, 50 wt.% and 70 wt.% biomass fibres were added (in relation to the solid matter content). The liquid to solid ratio was 1. After mixing, moulding and 1-day holding time, the specimens were heat treated at 60 °C for 6 hours.

The microstructures of the fly ash and lightweight samples were observed by Phenom ProX EDX electron microscope.

The wood, the fly ash and the fly ash-wood composite samples were investigated by JASCO FT/IR-4200 type Fourier transform infrared spectroscope. For the analyses, an FTIR Spectrometer equipped with a single-reflection diamond crystal was used. The spectra were collected in the absorbance range from 7800.65 to 349.053 cm^{-1} , at a resolution of 4 cm^{-1} . The spectra are baseline corrected.

Results and discussion

The characteristic particle sizes, geometric specific surface area (SSA) and loss on ignition (LOI) of the fly ash is summarised in Table 2. In case of the biomass samples (Figure 3), the maximum particle size was 10 mm.

Table 2. The characteristic particle sizes, SSA and LOI of the fly ash

	$x_{10}, \mu\text{m}$	$x_{50}, \mu\text{m}$	$x_{90}, \mu\text{m}$	SSA, cm^2/cm^3	LOI, %
Lignite FA	13.36	59.82	175.19	3148.78	0.37



Figure 3. The crushed woody biomass sample

In the SEM images seen in Figure4, spherical glassy particles – which are characteristic for fly ash – with hollow structure can be easily identified. The spherical particles may contain broken pores, in which smaller particles can be seen. Furthermore, irregular and needle-like shaped particles can also be observed.

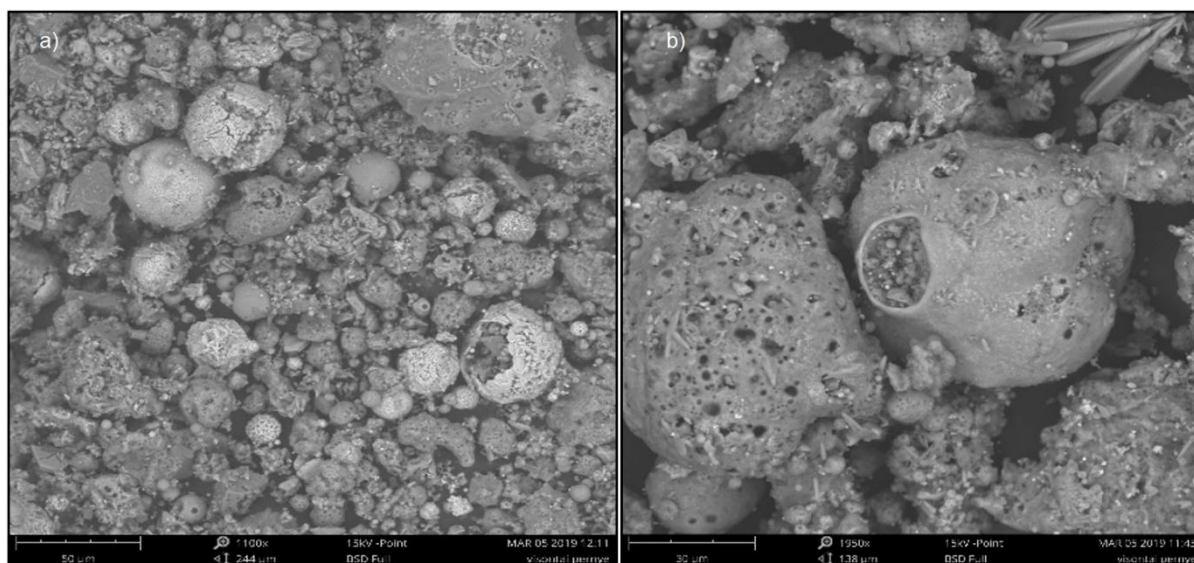


Figure 4. SEM images of raw fly ash with 1100x (left) and 1950x (right) magnifications

From the geopolymer-biomass mixture cylindrical specimens were produced (**Error! Reference source not found.**5), none of which showed breakage or crumbling during demoulding. Then the specimen densities were examined, the results of which are illustrated in Figure 6.

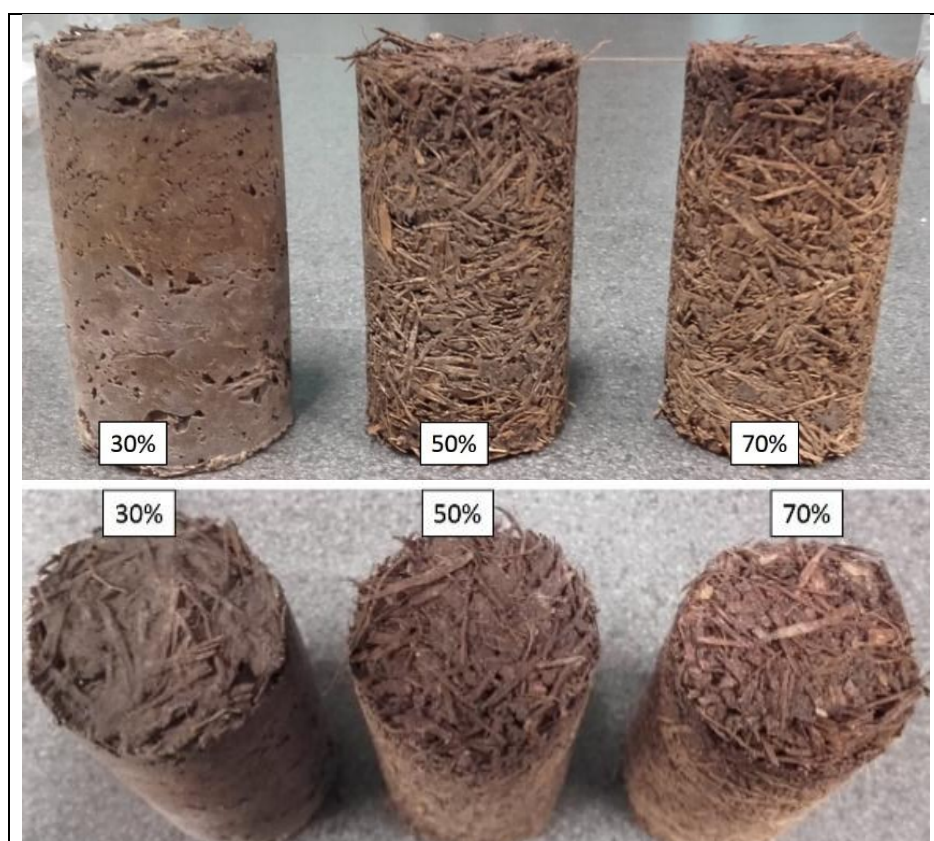


Figure 5. The geopolymer-biomass composite specimens

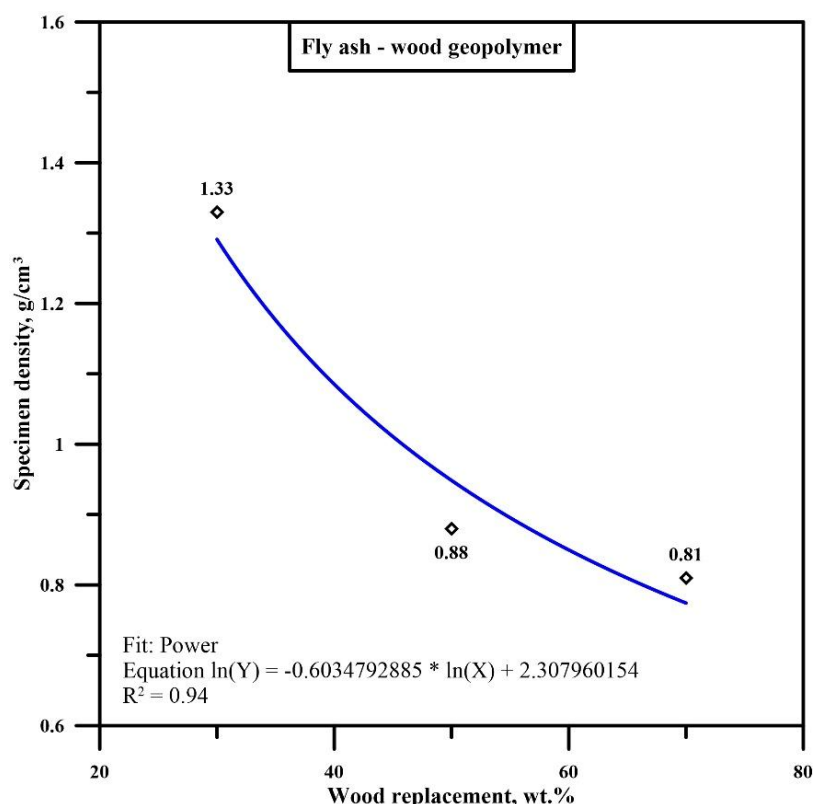
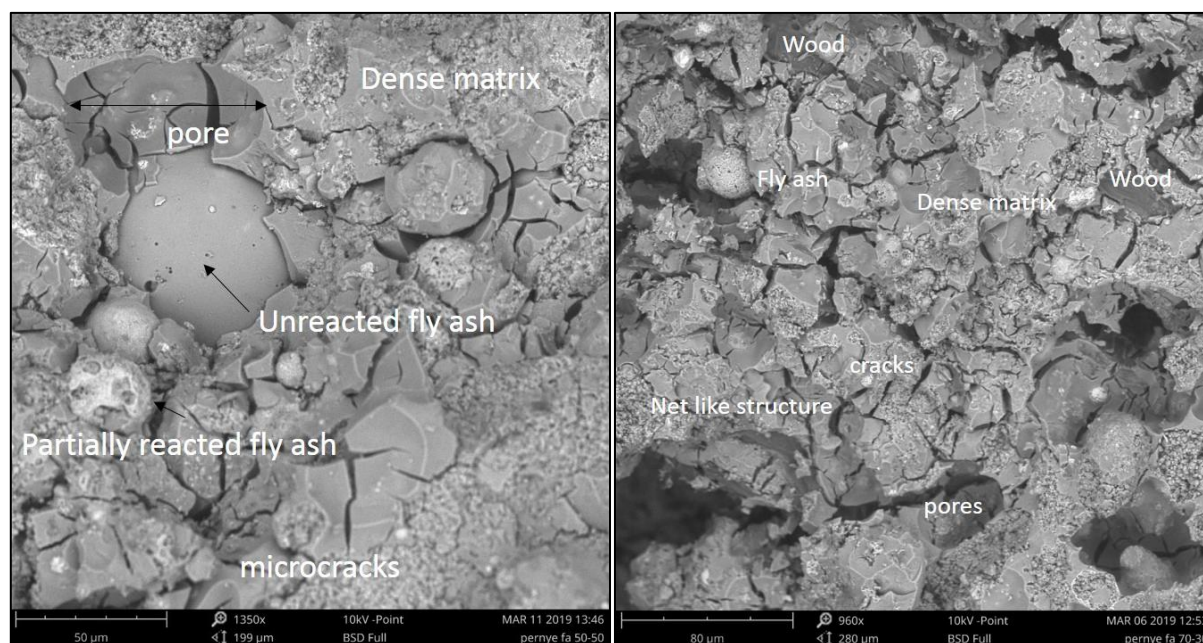


Figure 6. Specimen density of the geopolymer-biomass specimens

As it can be observed in Fig. 6, the specimen density showed a decreasing trend as the wood replacement in the specimens was increased. The average density with 30 wt.% wood was 1.33 g/cm³, which drastically decreased to 0.88 g/cm³ when the biomass content was increased to 50 wt.%. Further increasing the wood content resulted in slightly lower specimen density, with 0.81 g/cm³. Thus, with the addition of the woody biomass can be applicable for the production of a lightweight composite material.

SEM analysis was also performed on fly ash based geopolymers replaced with 30, 50 and 70 % wood particles by weight (Figure 7). The process of polycondensation caused porosity, resulting in decreased weight. The spherical fly ash particles are built into the amorphous geopolymeric framework of aluminosilicates. The composite contains undissolved solid particles of fly ash, or partially dissolved fly ash particles. The area of the unreacted particles is the most sensitive to mechanical loading. All samples with different replacement of wood shows microcracks which may result in lower compressive strength, and increased porosity. The SEM images indicate that there was good adhesion between the wood particles and the geopolymer matrix at the interface zone. The wood particles may bridge the micro and macro cracks of the brittle matrix. In case of 30% by weight replacement there are a lot of unreacted fly ash particles among the wood fibres, but with increasing amount of wood, the number of free fly ash particles decreased as they built into the geopolymeric gel. The fibres are covered with this newly formed dense fractured geopolymer gel. The surface of the dense geopolymer consists of a net like structure with pores, in which not reacted or partially reacted spherical fly ash particles can be observed.



a)

b)

Figure 7. SEM images of the (a) 50-50 (M=1350x) and (b) 70-30 (M=960) geopolymer biomass composites

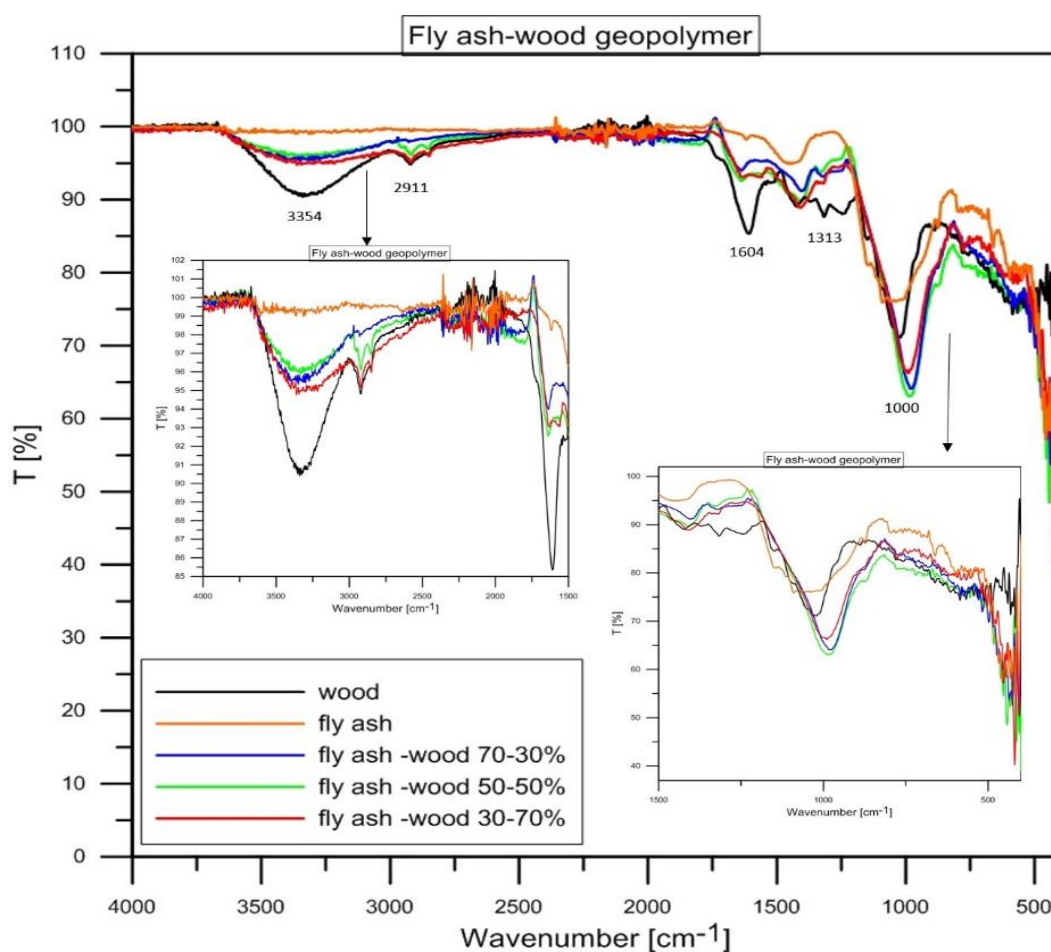


Figure 8. The FT-IR spectra of the base materials and the geopolymer specimens

The FT-IR spectra of the base materials and the geopolymers can be observed in Figure 8. The FT-IR spectrum of fly ash shows the main absorption band at about 1000 cm^{-1} due to the Si–O–Si and Al–O–Si asymmetric stretching vibration. The wood sample has a characteristic band at around 3354 cm^{-1} due to the O–H stretching which is due to the water content of the biomass [29]. The wood sample shows the characteristic bands of biomasses: hemicellulose can be found at the peak of 1710 cm^{-1} (unconjugated C=O in xylans), 1506 cm^{-1} is for aromatic skeletal in lignin and 1463 cm^{-1} is for the C–H deformation in carbohydrates and lignin. At 1343 cm^{-1} , the C–H deformation in cellulose and hemicellulose can be seen, the C–H in cellulose can be found at 1322 cm^{-1} , while the C–O stretch in lignin and xylan are at 1253 and 1230 cm^{-1} . 1128 cm^{-1} is for C–O–C vibration in cellulose and hemicellulose, 1128 cm^{-1} represents aromatic skeletal in lignin, and 883 cm^{-1} is for the C–H deformation in cellulose [30].

The addition of biomass fibres caused the main absorption band of fly ash to shift to lower frequencies in the geopolymer pastes. The band at about 1436 cm^{-1} appeared due to the stretching of the O–C–O bands, which may be the result of atmospheric carbonation of a highly alkaline NaOH aqueous phase, which was diffused on the geopolymeric material surface [29].

Conclusion

Based on the results, it can be stated that the received biomass fibres are compatible with the lignite fly ash geopolymer binder. Some of the possible application fields of the product may include the use as sound- and heat insulation material or lightweight composite. Systematic investigation to determine the optimal parameters and the effect on compressive and flexural performance should also be tested in the future.

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