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MECHANICAL AND STRUCTURAL PROPERTIES OF BIOMASS-GEOPOLYMER COMPOSITES

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Abstract: With the ever-increasing demand in the construction and building industry, not only the need for sustainable and environmentally friendly building materials but the application of locally available additive materials has been the focus of much research. Geopolymers are a novel material type, produced by the polycondensation and polymerisation of solid aluminosilicates by an alkali solution. Various geopolymer composites can be prepared with the addition of different artificial and natural materials, preparing for example fiber-reinforced or lightweight materials with increased heat, fire and acid resistance. Geopolymers are considered more environmentally friendly due to the lower CO₂ emissions during their production (compared to ordinary Portland cement), and the use of locally available natural materials to improve their properties can provide further benefits.

The examined geopolymer composites from woody biomass and fly ash based geopolymer were prepared with 25 wt.%, 50 wt.% and 75 wt.% biomass addition. The base materials exhibited good compatibility, especially between the fibrous phloem and the geopolymer matrix. The increased biomass content resulted in lowered flexural and compressive strength, but due to the decreased specimen densities, the application of the composites as lightweight construction material could be a feasible option.

Keywords: *biomass, fiber addition, fly ash, geopolymer composite, mechanical properties*

1. INTRODUCTION

Geopolymers are inorganic materials synthesized at room or elevated temperatures from solid silica and alumina containing primary or secondary raw materials in mainly alkaline and possibly acidic aqueous medium. During the geopolymerisation process, a 3D aluminosilicate framework is produced, creating the geopolymer matrix. The resulting material has numerous application fields, such as fire-resistant materials, thermal insulation, high-tech resins, toxic and radioactive waste containment, composites for the aircraft and automobile industries, etc. [1, 2].

Fly ash is a coal combustion product collected from flue gas by gas filtration equipment, which is mostly deposited into ponds for storage. Some possible utilizations include concrete production, mine reclamation, soil amendment, filler material

in road construction, etc. Furthermore, because of its high availability and possible reactivity, it has proven to be a suitable geopolymer base material, as well [3].

The addition of small quantities of natural fibers to reinforce both traditional cementitious materials and geopolymers has proven to be suitable to improve the mechanical properties of the brittle cementitious matrices. Some of the examined geopolymer composites have included the addition of cotton [4, 5], wool [6, 7], sawdust [8], sisal [9, 10], coconut [11], and bamboo fibers [12].

In this article, the results of the examination of woody biomass–flyash based geopolymer composites are summarized. The flexural and compressive strength, specimen density, structural changes, and microstructural properties were analyzed.

2. MATERIALS AND METHODS

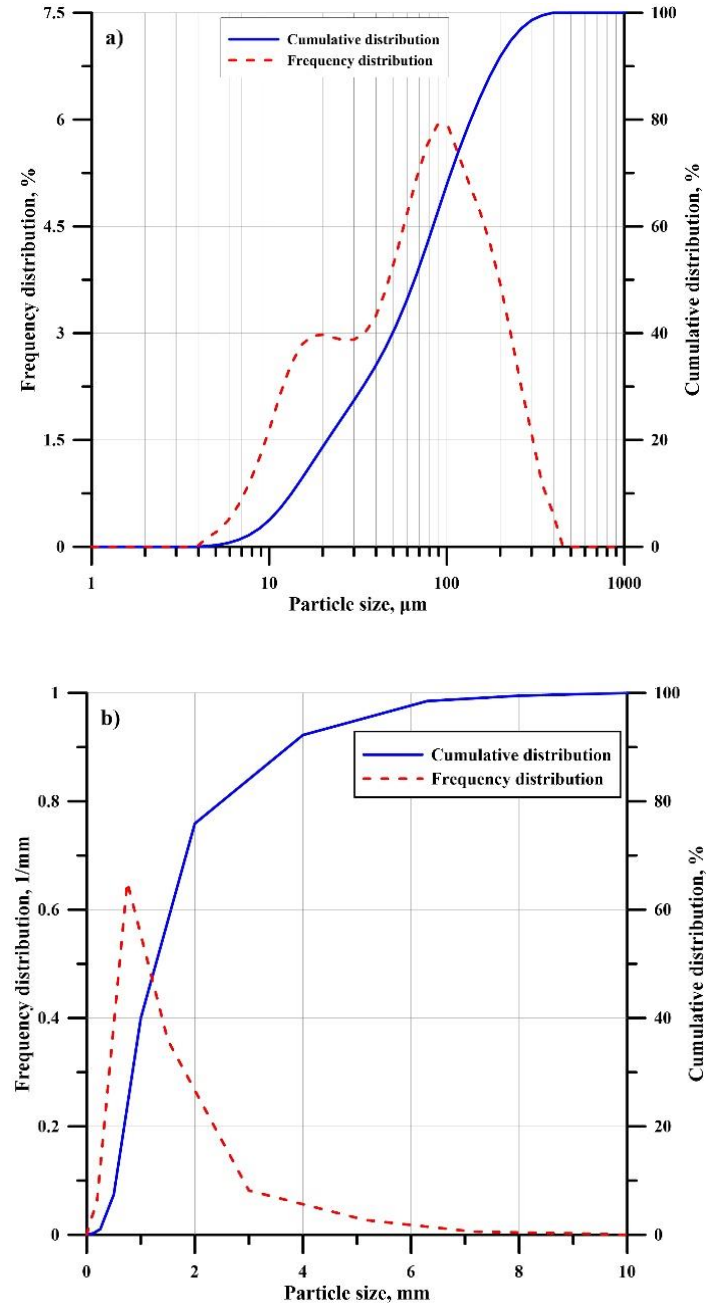
2.1. Base materials

The woody biomass was from an approximately 45-to-60-year-old linden (*Tilia*) tree, originating from the Botanical Garden of the University of Sopron, collected in 2018. The diameter of the logs was 30–40 cm. After separating the cork and phloem from the wood, the fiber production was carried out with hammer mill with a screen size of 10 mm.

The lignite fly ash was collected from Mátra Power Station. Before use, the sample was dried at 105 °C then sieved to remove >1 mm particles, such as unburned coal, slag and other contaminants. The moisture content of the fly ash was 25.0% and the loss on ignition was 0.37 wt.%. The particle and bulk densities were 1.84 g/cm³ and 0.63 g/cm³, respectively.

The cumulative and frequency distributions of the fly ash particles were analyzed with a Horiba LA-950 V2 laser particle size analyzer (*Figure 1a*). The characteristic particle sizes were $x_{10} = 13.36 \mu\text{m}$, $x_{50} = 65.78 \mu\text{m}$ and $x_{90} = 187.18 \mu\text{m}$. In the frequency curves, two local maximum points can be observed, at $\sim 11 \mu\text{m}$ and $\sim 100 \mu\text{m}$. The geometric specific surface was calculated by the particle size analyzer to be 956.02 cm²/g. The BET specific surface was measured using a Gemini VII 2390 Series Surface Area Analyzer, the value was 14.68 m²/g.

In case of the woody biomass, the cumulative and frequency distributions (*Figure 1b*) were measured with sieve analysis. According to the frequency distribution, the 0.5–1 mm size fraction contained the highest amount of sample, with considerable amounts from both the friable cork and the fibrous phloem.

**Figure 1**

Cumulative and frequency distribution curves: a) fly ash; b) biomass

2.2. Geopolymer mixtures

The biomass and fly ash were mixed in three ratios: 25 wt.% biomass – 75 wt.% fly ash, 50 wt.% biomass – 50 wt.% fly ash and 75 wt.% biomass – 25 wt.% fly ash.

The activator solution consisted of 27 wt.% 8 M NaOH solution and 75 wt.% water glass with the following composition: 25.3% SiO₂, 13.7% Na₂O, 2.7% K₂O and 48.3% H₂O.

The liquid-to-solid ratio was 1 : 1.

During geopolymer production, the fly ash was mixed with the activator solution before the woody biomass addition. The mixtures were poured into molds and homogenized for 1 minute using a vibrating table. After a 1-day aging under sealed conditions, the specimens were heat treated at 60 °C for 6 hours. The cooled down geopolymer composites were held under sealed conditions for an additional 5 days before the strength measurements of the 7-day-old specimens could be carried out.

2.3. Test methods and apparatus

For flexural strength tests, the dimensions of the specimens were 40 × 40 × 160 mm, while the compression strength test bars were of 60 mm height and 40 × 40 mm cross-section. The flexural and compression strength tests were carried out using three and six specimens, respectively, based on the standard MSZ EN 196-1:2016 at the age of 7 days.

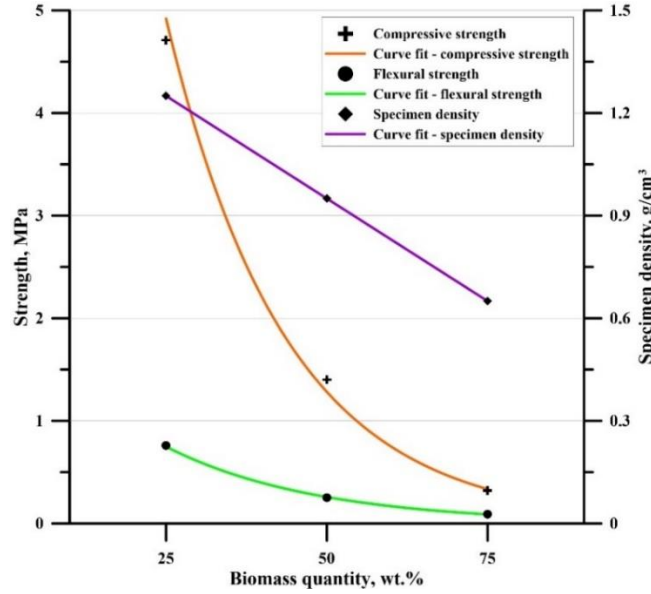
Microstructural analyses on fly ash-biomass composites were performed by Fourier transform infrared spectroscopy (FT-IR), where stretching and bending vibrations of chemical bonds of functional groups in samples were detected by JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in reflection mode, with diamond ATR. The infrared transmission spectra of samples were recorded for 400–4000 cm⁻¹ at spectral resolution of 4 cm⁻¹ using a Perkin-Elmer spectrum to measure the absorption spectra of the bonds. The spectrum is baseline corrected.

The morphology of the fly-ash based geopolymer replaced by biomass was observed by Phenom ProX electron microscopy equipped with EDS detector. The fly ash–biomass composite samples after compressive strength measurement were stacked onto the carbon adhesive. The measurement conditions include accelerating voltage 10 and 15 kV, in point analysis mode with spectrum collection time of 60 s. The images were taken at varying magnification.

3. RESULTS

3.1. Strength and specimen density values

The results of the flexural and uniaxial compressive strength, and the specimen density measurements are summarized in *Figure 2*, with the fit curves to each test result.

**Figure 2**

Results of strength and specimen density measurements

With 25 wt.% biomass addition, the flexural strength was 0.75 MPa, which decreased to 0.25 MPa and 0.09 MPa as the biomass quantity was increased. The decrease in the flexural strength can be described with $R^2 = 0.997$ using Equation (1). During the flexural strength tests, the specimens failed to break after reaching the breaking point, exhibiting the flexible behavior characteristic to fiber-reinforced geopolymer. However, the decreasing flexural strength hinders the applicability of the composites as fiber-reinforced building material.

$$y = -0.043x + 0.777 \quad (1)$$

For the compressive strength the same tendency could be observed, as the highest uniaxial compressive strength was 4.71 MPa, achieved with 25 wt.% biomass. With higher biomass content, the strength values exponentially decreased to 1.40 MPa with 50 wt.%, and 0.32 MPa with 75 wt.% biomass. The strength decrease can be characterized by Equation (2), the $R^2 = 0.999$. The decrease in the uniaxial compressive strength values can be explained by the higher amount of geopolymer matrix in the composites with lower biomass quantity, which provides the dense structure and strength to the samples.

$$y = -0.054x + 2.938 \quad (2)$$

Increasing the amount of biomass in the composites led to linear decrease in the specimen density values [Equation (3), $R^2 = 1$]. The initial 1.25 g/cm^3 was decreased to 0.95 g/cm^3 , then 0.65 g/cm^3 with the addition of biomass. This can be due to the density difference between the fly ash and the woody biomass: the higher the amount of lower density biomass in the composites (as a replacement of the higher density fly ash), the lower the density becomes.

$$y = -0.012x + 1.55 \quad (3)$$

Based on the strength and specimen density results, it can be concluded that even though the addition of high quantity of woody biomass decreased the flexural and uniaxial compressive strength of the specimens, due to the decreased specimen density, the production of a lightweight building material from the biomass-geopolymer composite could be a potential area of utilization. However, further experiments should be conducted to confirm the applicability of the prepared materials.

3.2. Microstructural analysis

FT-IR

First, we measured the spectra of the raw materials to compare the structural changes caused by alkali activation. Wood fiber consists of mainly cellulose, hemicellulose and lignin. Cellulose is a linear polymer which is insoluble in water and is the main component of wood fiber, forming the frame of the cell wall. Hemicellulose and lignin form the surrounding intercellular substance. Hemicellulose is chemically polysaccharide of low molecular weight, so it can be dissolved in water. Lignins are polymeric aromatic constituents in plant cell walls, which bond fibers and give stiffness to wood. Hemicellulose and cellulose are mainly composed of oxygen functional groups which are present in the lignocellulose material such as hydroxyl, ether, carbonyl, while lignin is a complex, systematically polymerized, highly aromatic substance and acts as cementing matrix that holds between and within both cellulose and hemicellulose units. Wood fibers can be used in various forms as reinforcement. The FT-IR spectra of the raw materials can be seen in Figure 3. The biomass shows strong broad overlapping bands between $3654\text{--}2721 \text{ cm}^{-1}$. The main band of the wood spectra centered at 3329 cm^{-1} indicates the OH stretching vibration in hydroxyl groups, which all main wood components contain. The smaller band at 2915 cm^{-1} and 2849 cm^{-1} can be derived from asymmetric C-H and symmetric C-H bonds, present in cellulose and hemicellulose. The strong band at 1604 cm^{-1} indicates the bonding of C = C or C = N. The band at 1413 cm^{-1} can be ascribed as O-H vibrations and C = O vibrations in cellulose. The C-O carbonyl band in lignin and xylan units was observed at 1229 cm^{-1} . The main absorption band centered at 1034 cm^{-1} is a superposition of broad overlapping bands coming from the C-O stretching vibration of cellulose, hemicellulose and lignin. The absorption bands from 900 to 400 cm^{-1} region are strongly reduced in intensity. The band at 837 cm^{-1} is assigned to C-O-C stretching as an amorphous absorption band.

In the case of fly ash, small bands at 1614 cm^{-1} correspond to the H-O-H bending vibrations. The peak identified at 1465 cm^{-1} can be related to the O-C-O stretching vibration of a carbonate phase. The main absorption band is located between 1270 and 833 cm^{-1} and is attributed to the Si-O-Al and Si-O-Si asymmetric stretching vibrations. The band at 812 cm^{-1} is attributed to the bands present in the fly ash source as quartz or mullite. The peak at 559 cm^{-1} is assigned to the Si-O-Al bending vibration. Bands with low intensity at the low wavenumber side belong to Si-O Si-O-Si bending vibrations [13].

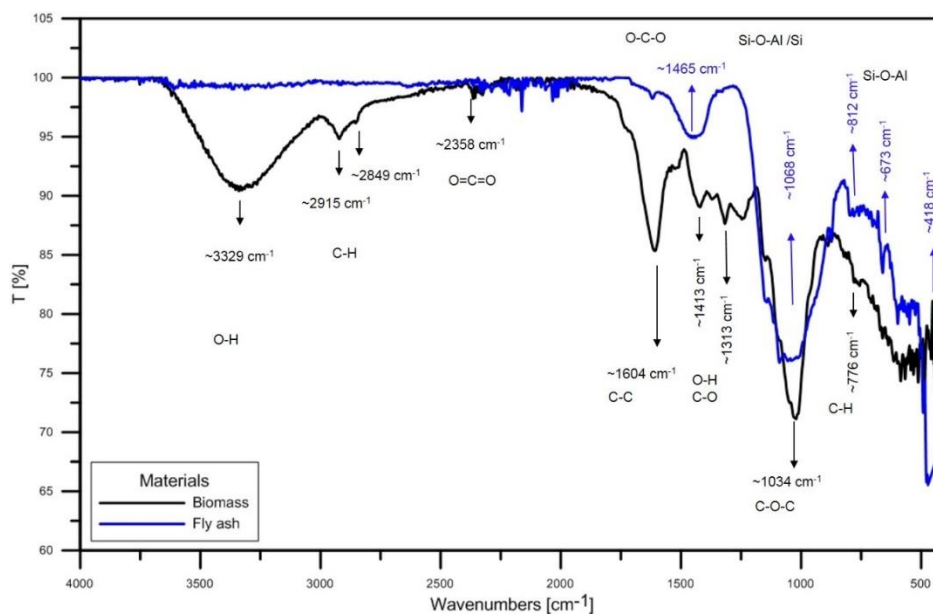


Figure 3
FT-IR spectra of the raw materials (wood fibers and fly ash)

As is illustrated in *Figure 4*, after alkali activation of the fly ash based geopolymer replaced by 25 wt.% biomass, the spectrum shows a new band at 1700 cm^{-1} derived from the C = O vibrations of biomass. The band of fly ash shifts from 1465 cm^{-1} to 1401 cm^{-1} , which might be formed from remaining unreacted activator and CO_2 . The main absorption band located at 1068 cm^{-1} shifts to 979 cm^{-1} with the replacement of biomass. The bands of fly ash between 800 cm^{-1} and 500 cm^{-1} coming from Si-O-Al decreases significantly, which may indicate reaction. The most obvious changes of the absorption band of the composite are the disappearing of the O-H stretching band at 3329 cm^{-1} and the small C-H bands at 2915 cm^{-1} and 2849 cm^{-1} coming from the biomass. The increasing portion of biomass shows absorption bands at 3310 cm^{-1} , 2922 cm^{-1} , and 2360 cm^{-1} that can be derived from the biomass. In the case of 50 wt.% replacement the band of C-O centered at 1401 cm^{-1} shows the most intense absorption band of all of the composites, indicating the highest amount of carbonate formation due to the alkali activation. The intensity of the main Si-O-Al band decreases as the

fly ash content decreases. At the low wavenumber side of the spectra the biomass derived amorphous absorption band become more intense. The replacement of fly ash with 75 wt.% biomass shows a band at 979 cm^{-1} with the lowest intensity due to the low proportions of fly ash.

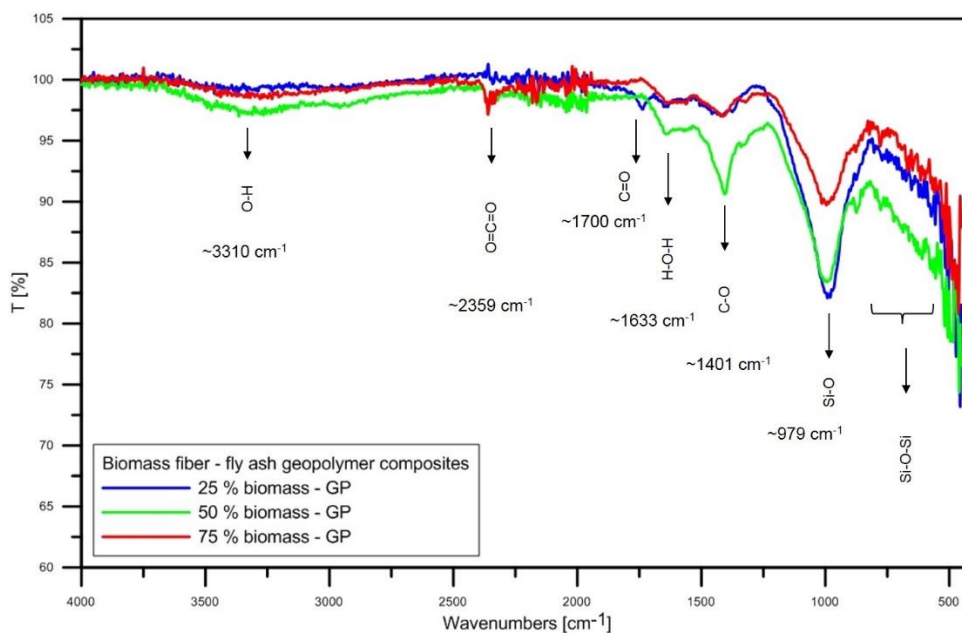


Figure 4
*FT-IR spectra of the fly ash based geopolymer
with different portions of wood fibers*

Scanning electron microscopy

The analysis was performed first on raw fly ash then on fly-ash based geopolymer replaced by 25, 50 and 75 wt.% crushed wood fibers. *Figure 5* shows raw fly ash particles with spherical shapes and smooth surfaces of different sizes. Most particles are hollow and filled with fragments.

The fly ash biomass composites were compact, with micro-porosity and holes formed during polycondensation. Both fly ash and wood particles underwent significant changes of morphology and chemical composition in the geopolymer due to the alkali reaction. The spherical fly ash particles are built into the amorphous geopolymer framework of aluminosilicate. The composite contains undissolved solid particles of fly ash with higher amounts of Si, Al, and Fe, or partially dissolved fly ash particles. In *Figure 5*, partially reacted fly ash particles can be seen. The area of the unreacted particles is the most sensitive to mechanical loading. All of the samples with different replacement of biomass show micro cracks, which resulted in lower compressive strength, and increased porosity. The micro cracks could have formed

as a result of drying of geopolymer concrete specimens. The strong chemical bond between the geopolymer gel and wood fiber can be the main reason for higher flexural and compressive strength.

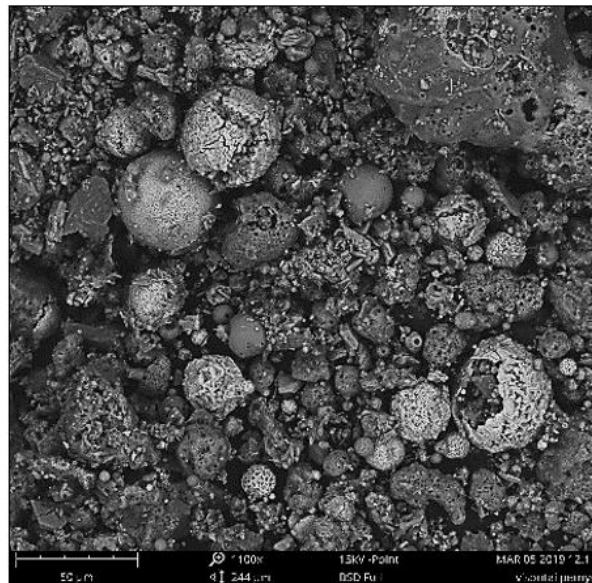
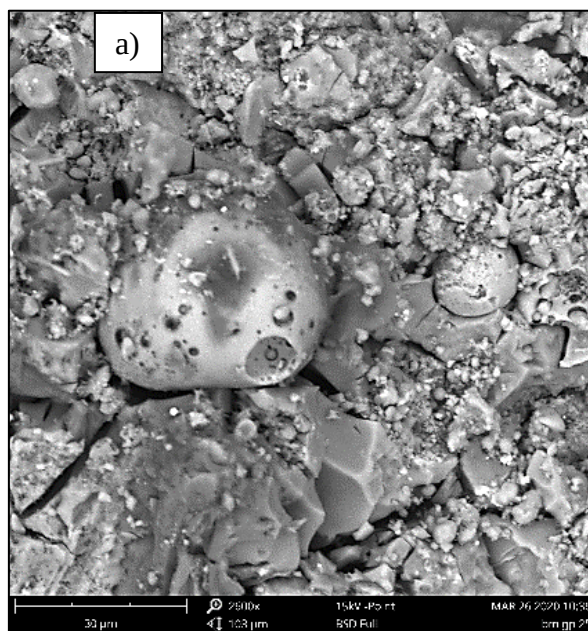


Figure 5

Fly ash with its spherical particles (Sample from Visonta, Mátra Power Plant)



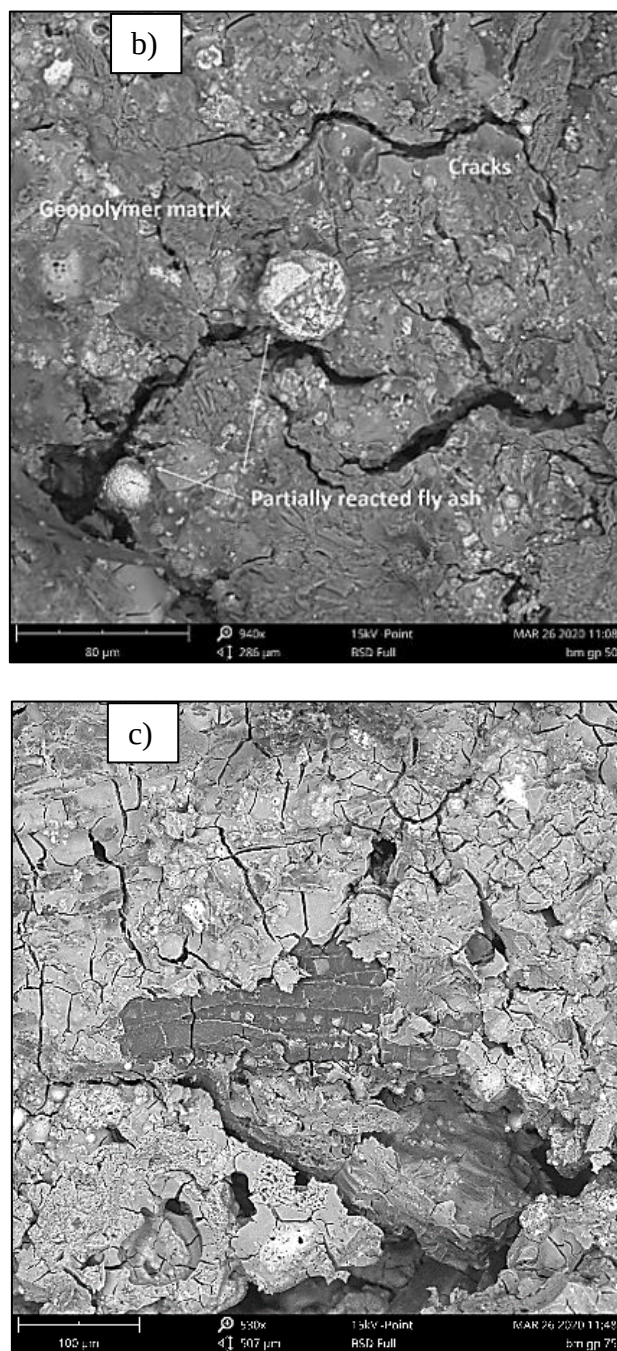


Figure 6

Microstructure of the fly ash based geopolymer replaced by 25 wt.% wood (a), 50 wt.% wood (b) and 75 wt.% wood fibers (c)

The SEM images in *Figure 6* indicate that there was good adhesion between the fibrous 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 the case of 25% by weight replacement there were unreacted fly ash particles among the wood fibers, but with an increasing amount of wood, the number of fly ash particles decreased as they built into the geopolymer gel (50 wt.% replacement). The fibers are covered with this newly formed geopolymer gel binding the fibers together. In the case of 75 wt.% replacement the wood fibers are covered with dense, fractured geopolymer gel, but the fibers were not bound together due to the low amount of fly ash meaning low compressive strength.

Table 1
The results of EDS analysis in the case of geopolymer and wood fiber

Element	Weight concentration (%)	
	Geopolymer	Wood fiber
Oxygen	30.18	43.98
Silicon	29.83	2.3
Calcium	12.89	0.55
Carbon	7.4	46.72
Sodium	6.72	5.16
Potassium	5.06	0.39
Aluminum	4.14	0.44
Sulfur	1.83	0.09
Iron	1.68	0.3
Magnesium	0.26	0.06

The data from the elemental analysis of the geopolymer gel and the uncoated wood surface are summarized in *Figure 7* and *Table 1*. The composition of the geopolymer gel contains high amount oxygen, silicon and calcium, which is a part of the C-S-H (calcium-silicate-hydrate) gel responsible for mechanical properties in the fly ash biomass composite. The potassium and sodium content of the geopolymer originates from the alkali solution of NaOH and water glass mixture, while the rest of the trace elements, i.e. sulfur, iron, etc., correspond to the composition of the fly ash used. The chemical composition of the biomass fiber consists of mainly C and O with a low amount of Na. The lack of H in the EDS analysis data is due to the inability of the instrument to identify hydrogen during the analysis. The polygonal structured part of the wood (cork) is not appropriate for geopolymer gel formation, as proved by the lack of geopolymer on its surface with a trace amount of Si, Al and Ca, which are more dominant in the geopolymer gel.

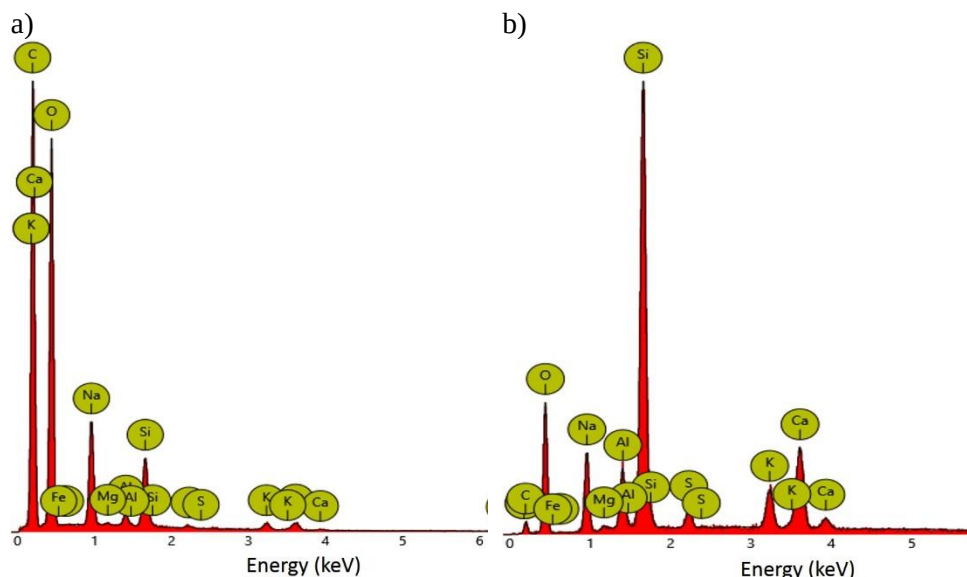


Figure 7

The spectrum of a) the geopolymer gel and b) the wood fiber after alkali activation

4. CONCLUSIONS

In the article, experimental results of biomass-geopolymer composites were presented, with 25 wt.%, 50 wt.% and 75 wt.% woody biomass addition to fly ash based geopolymer. The flexural and uniaxial compressive strength test values of the specimens could be described with exponential decrease as the biomass quantity was increased in the geopolymer matrix. The specimen density of the specimens linearly decreased as the higher density fly ash was replaced with lower density biomass. The main components of the base materials could be identified by the FT-IR analysis and the shifts of bands in the spectra of the composites indicated the geopolymerization reaction. As the biomass quantity was increased in the composites, the bands corresponding to the biomass became more dominant in the spectra. The SEM images showed unreacted fly ash particles in all three composite samples, along with micro cracks on the geopolymer structure. The fibrous phloem of the woody biomass was coated with the geopolymer gel, while the friable cork part was not compatible with the geopolymer matrix. Based on the results of the microstructural analysis and the strength tests of the biomass-geopolymer composites, it can be concluded that cork of the sample mainly acts as filler in the composite.

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REFERENCES

- [1] Davidovits, J. (1991). Geopolymers: Inorganic polymeric new materials. *Journal of Thermal Analysis*, 37, pp. 1633–1656, DOI: 10.1007/BF01912193.
- [2] Zhuang, X. Y., Chen, L., Komarneni, S., Zhou, C. H., Tong, D. S., Yang, H. M., Yu, Hao Wang, W. H. (2016). Fly ash-based geopolymer: clean production, properties and applications. *Journal of Cleaner Production*, 125, pp. 253–267, DOI: 10.1016/j.jclepro.2016.03.019.
- [3] Nath, S. K., Kumar, S. (2019). Reaction kinetics of fly ash geopolymerization: Role of particle size controlled by using ball mill. *Advanced Powder Technology*, 30 (5), pp. 1079–1088, DOI:10.1016/j.appt.2019.02.003.
- [4] Alomayri, T., Shaikh, F. U. A., Low, I. M. (2014). Synthesis and mechanical properties of cotton fabric reinforced geopolymer composites. *Composites Part B: Engineering*, 60, pp. 36–42, DOI: 10.1016/j.compositesb.2013.12.036.
- [5] Alomayri, T., Shaikh, F.U.A., Low, I. M. (2013). Thermal and mechanical properties of cotton fabric-reinforced geopolymer composites. *Journal of Materials Science*, 48, pp. 6746–6752, DOI: 10.1007/s10853-013-7479-2.
- [6] Alzeer, M., MacKenzie, K. J. D. (2012). Synthesis and mechanical properties of new fibre-reinforced composites of inorganic polymers with natural wool fibres. *Journal of Materials Science*, 47, pp. 6958–6965, DOI: 10.1007/s10853-012-6644-3.
- [7] Ranjbar, N., Zhang, M. (2020). Fiber-reinforced geopolymer composites: A review. *Cement and Concrete Composites*, 107, p. 103498, DOI: 10.1016/j.cemconcomp.2019.103498.
- [8] Duan, P., Yan, C., Zhou, W., Luo, W. (2016). Fresh properties, mechanical strength and microstructure of fly ash geopolymer paste reinforced with sawdust. *Construction and Building Materials*, 111, pp. 600–610, DOI: 10.1016/j.conbuildmat.2016.02.091.
- [9] Da Silva Alves, L. C., dos Reis Ferreira, R. A., Bellini Machado, L., de Castro Motta, L. A. (2019). Optimization of metakaolin-based geopolymer reinforced with sisal fibers using response surface methodology. *Industrial Crops and Products*, 139, p. 111551. DOI: 10.1016/j.indcrop.2019.111551.
- [10] Silva, G., Kim, S., Aguilar, R., Nakamatsu, J. (2020). Natural fibers as reinforcement additives for geopolymers – A review of potential eco-friendly

- applications to the construction industry. *Sustainable Materials and Technologies*, 23, e00132, DOI: 10.1016/j.susmat.2019.e00132.
- [11] Korniejenko, K., Frączek, E., Pytlak, E., Adamski, M. (2016). Mechanical properties of geopolymer composites reinforced with natural fibers. *Procedia Engineering*, 151, pp. 388–393, DOI: 10.1016/j.proeng.2016.07.395.
- [12] Sá Ribeiro, R. A., Sá Ribeiro, M. G., Sankar, K., Kriven, W. M. (2016). Geopolymer-bamboo composite – A novel sustainable construction material. *Construction and Building Materials*, 123, pp. 501–507, DOI: 10.1016/j.conbuildmat.2016.07.037.
- [13] Pandey, K. K., and Pitman, A. J. (2004). Examination of lignin content in a softwood and a hardwood decayed by a brown-rot fungus with acetyl bromide method and Fourier transform infrared spectroscopy. *Journal of Polymer Science Part A – Polymer Chemistry*, 42, pp. 2340–2346. DOI: 10.1002/pola.20071.