Tribo-Mechanical Behavior of Geopolymer Composites with Wasted Flax Fibers

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Abstract. The paper presents the research results on the mechanical and tribological properties of geopolymers reinforced with natural fibers. As a matrix, conventional fly ash and dry construction sand in proportion 1:1 were used. Materials were activated with Na activator. Wasted flax tow in an amount of 0.25-1% by weight was introduced as a reinforcement. The test results showed that with the increase in the fiber content, the bending strength increases, while the compressive properties are comparable to the matrix material. Based on the obtained research results, the optimal content of flax tow was determined at the level of 0.5% by weight. In addition, the abrasion resistance of geopolymer composites was determined using the so-called Boehme shield. This test consists of measuring the change in sample height. The sample is placed on a disc sprinkled with abrasive powder, then pressed and put into rotation. The abrasion results showed that the addition of fibers in the form of waste pulps does not reduce the abrasion resistance, which should be considered as a positive effect. Research also revealed that wasted flax fibers could be successfully used as a reinforcing material in geopolymeric materials as an alternative to the utilization of waste fibers, and additionally may also have a positive effect on the mechanical and tribological properties of geopolymers materials.

1. Introduction

The term "geopolymers" refers to inorganic polymers, which are amorphous aluminosilicate materials synthesized in a strongly alkaline environment at a temperature up to 100° C. The structure of geopolymers is very similar to natural stones, which is why they are often called "artificial stones". Geopolymers consist of long chains - copolymers of aluminum and silicon oxides, as well as metallic cations and bound water that stabilize them. In addition to well-defined polymer chains, the material usually contains various mixed phases, such as silicon oxide, unreacted aluminosilicate substrate, and sometimes crystallized zeolite-type aluminosilicates [1-2].

Geopolymer materials are of great interest to scientists, and many studies have already been published on this topic. In the analysis of the available literature, the most widely conducted works were on the use of fly ash, metakaolin, rice husk ash, or slag for the production of geopolymer or alkali-activated materials. Published studies indicate that geopolymer materials show excellent mechanical strength and durability, resistance to a corrosive environment, and very high temperatures, makes them materials that show great potential in construction applications [3-12].
However, geopolymeric materials have disadvantages, one of them is a low fracture toughness and thus a reduction in strength properties. The solution to this problem is, for example, the introduction of reinforcing fibers, which can significantly reduce the propagation of cracks [13], hence the research on geopolymer composites reinforced with short fibers [14]. The commonly used fibers in geopolymer matrices include organic, inorganic, and natural fibers. Polyethylene, polypropylene, and aramid fibers are used as organic fibers, steel and carbon fibers are among the inorganic fibers. The advantage of organic and inorganic fibers is their high mechanical strength and repeatability compared to natural fibers [15-17]. However, natural fibers are getting more popular; for example, applied natural fibers are flax, sisal, banana, coconut, cotton, raffia, jute, and basalt fibers. These fibers are mainly introduced to increase the resistance to tensile and compressive stresses [2].

Due to the increasing environmental burden, research was also undertaken on the use of waste materials as reinforcement in geopolymer composites. Examples of such fibers are rockwool waste or waste cotton stalk materials. Research has shown that non-recyclable waste can be a valuable raw material for producing geopolymeric materials [18-19].

This paper presents the basic tests of the strength and wear properties of geopolymer composites reinforced with waste flax fibers to indicate the potential of using waste fibers as an alternative to the standard thermal utilization process. This research aimed to emphasize the principle that should be followed when making decisions regarding appropriate methods and technologies of waste disposal. It is, the principle of sustainable development helps in proper waste management, and such management aims to consider economic and environmental aspects while using waste in the widest possible use.

2. Materials and Methods

2.1. Materials

The geopolymer matrix was made of fly ash from the Skawina CHP Plant (Skawina, Poland) and a fine dry saturated construction sand at a ratio of 1:1. The fly ash applied in this study is composed mainly of silica and alumina and includes less than 4% calcium oxide [2]. The precise proportion of each phase in the fly ash is presented in Table 1. Based on an analysis of the diffraction patterns, it can be concluded that the conventional fly ash was characterized by a high quartz content, mullite, hematite, and alite. These are the most important components that react in the geopolymerization process [21]. In the microscopic photo (Figure 1), globular fly ash particles up to 20 μm in size (point no. 1), unburned carbon (point no.2), as well as particles containing high contents of aluminum and silicon oxide, which was confirmed in the EDS analysis can be seen. Spectrometric analysis showed that the fly ash contains silicon, aluminum, and calcium compounds and low iron content, which positively affects the geopolymerization process.

| Sample ID | Identified phases | Chemical formula |
|-----------|------------------|------------------|
| Fly ash   | Quartz           | SiO₂             |
|           | Mullite          | Al₆Si₂O₁₃        |
|           | Hematite         | Fe₂O₃            |
|           | Alite            | Ca₃SiO₅          |
Flax tow (Hempiflax Group Sp. Z o.o., Cracow) was used to reinforce geopolymer composites. The reinforcement was added in the amount of 0.25% (sample designated as 0.25W), 0.5% (0.5W), 0.75% (0.75W) or 1% (1W) by weight of dry components (Table 2). For comparison, a reference sample based on matrix material without any additives was made (samples designated as BM).

A 10 molar (10 M) solution of sodium hydroxide and sodium water glass R-145 (with a molar modulus of 2.5 and a density of about 1.45 g/cm$^3$) were combined as an alkaline activator in the ratio of 1:2. The alkaline solution was prepared by pouring the aqueous sodium silicate solution into flakes of technical sodium hydroxide dissolved in water. The solution was mixed and allowed to reach equilibrium concentration and ambient temperature. The fly ash, construction sand, flax tow, and alkali solution were mixed to form a homogeneous paste for about 15 minutes in a slow-speed mixing machine to prepare the geopolymer masses.

In the next step, the prepared masses were poured into molds, which were vibrated on a vibrating table to remove air bubbles. The tightly wrapped foil molds were heated at 75°C in a laboratory dryer for 24 hours. The samples were unmolded and stored under laboratory conditions (temperature about 20 °C, relative humidity about 50%). After 28 days, mechanical tests were done.

### Table 2. Designation of the manufactured composites.

| Index | Mixture Proportion (% by Weight) | NaOH Solution | Density (g/cm$^3$) |
|-------|---------------------------------|---------------|-------------------|
|       | Fly Ash | Sand | Flax tow | 10 M sodium hydroxide solution + water glass (1200 mL in total) | 1.81 ± 0.06 |
| BM    | 50      | 50   | -       | 1.83 ± 0.03       |
| 0.25W | 49.87   | 49.87| 0.25    | 1.79 ± 0.05       |
| 0.5W  | 49.75   | 49.75| 0.5     | 1.71 ± 0.08       |
| 0.75W | 49.62   | 49.62| 0.75    | 1.65 ± 0.1        |
| 1W    | 49.5    | 49.5 | 1       |                   |

### Methods

#### 2.2.1. Density

Before performing the strength tests, the density of the samples was determined using a geometric method. The density of each geopolymer composition was determined as the average of the four measurements. The samples were dimensioned with a laboratory caliper with a measurement accuracy of 0.01 mm. The weight of the samples was measured with a laboratory precision analytical scale RADWAG PS 200/2000.R2 (maximum load: 200/2000 g; reading accuracy: 0.001 / 0.01 g).
2.2.2. X-ray diffraction (XRD) and microscopic analysis

X-ray diffraction (XRD) was carried out with an X’Pert Pro MPD diffractometer (PANalytical, Malvern, UK) with CuKα radiation at 30 mA and 40 kV. The 2θ angle was varied from 20 ° to 53 ° with a step of 0.04 ° and an accumulation time of 7 s for each step.

Microscopic observations and energy dispersive spectroscopy (EDS) were conducted using a scanning electron microscope Joel JSM-820 with the EDS (IXRF, Inc., Austin, TX, USA) X-ray detector.

2.2.3. Strength tests

Compressive strength tests were performed according to EN 12390-3 standard ("Testing of hardened concrete. Compressive strength of specimens"). The tests were performed on a Matest 3000 kN universal testing machine (Matest, Treviolo, Italy) with a speed of 0.05 MPa/s. The dimensions of the specimens are according to EN 12390-3 (approximately) 50 mm × 50 mm × 50 mm.

Flexural strength tests were also performed according to the EN 12390-5 standard ("Hardened concrete tests. Flexural strength of test specimens"). Tests were also performed on a Matest 3000 kN universal testing machine with a speed of 0.05 MPa/s. Prismatic specimens with dimensions approximately 50 mm × 50 mm × 200 mm were made according to EN 12390-5.

2.2.4. Abrasive wear test

Abrasion tests were carried out using the Boehme shield method according to the PN-EN 13892-3: 2005 standard. For the test, samples with dimensions of 71 mm x 71 mm x 71 mm were prepared, the initial dimensions were measured with a caliper, and then the sample was placed in the holder of the device, and pressure equal to 294N was applied. Corundum powder was used as the abrasive, four grinding cycles were carried out for 22 turns each. After each cycle, the sample was rotated by 90° to eliminate abrasion unevenness.

3. Results and discussions

Table 2 shows the density results of the produced composites. Along with the increase in the share of fibers, the density of the composite decreases, which is related to the lower density of the flax fibers, the density of which is 1.37 g / cm3 [20]. Figure 2 shows a histogram of particle size distribution and cumulative particle size distribution curve for the fly ash used in the test. Figure 3 presents a histogram of the particle size distribution for the construction sand. The sieve analysis results showed that fly ash consisted of particles below 200 microns in the amount of about 80%, including particles below 100 micrometers about 30%, and particles above 200 microns constituted about 12%. Diaz et al. studied factors impacting the suitability of fly ash as a source material for geopolymers, including the effect of fly ash particle size on geopolymer properties. The study showed that particle size distribution is one of the most relevant physical properties that affect the reactivity of fly ash and the subsequent geopolymer product. Since much of the reaction proceeds at the particle-liquid boundary, the finer the particles, the larger the surface area and the higher the reactivity of the fly ash [21]. The addition of sand to geopolymeric materials is justified to increase the strength. Kuenzel et al. proved that the addition of sand increases the viscosity of the paste. The mechanical strength increases significantly when the sand content is above 25% by volume. In addition, the sand reduces the formation of cracks due to significantly lower linear shrinkage. It is related to the formation of a supporting network with a predetermined void volume. The higher the sand content, the higher the compressive properties [22].
Figure 2. Histogram of particle size distribution and cumulative particle size distribution curve for the fly ash used in the test

Figure 3. Histogram of particle size distribution and cumulative particle size distribution curve for the construction sand used in the test

Much attention has been devoted to the mechanical and physical properties of fiber-reinforced composites, which are greatly influenced by the type, quantity, and morphology of the reinforcing fibers and the interfacial bonding efficiency between the fibers and the matrix of the composite. Variables such as fiber content, orientation, aspect ratio, and interfacial strength are essential to the final balance of composite strength properties. The addition of short fibers to geopolymeric materials leads to composites that show significant improvements in mechanical properties such as bending and compression strength. The next stage of the research was to determine the strength properties during the flexural and compression test. Both the bending and the compressive strength increased with increased
waste fiber content, although the improvement was more noticeable in the bending strength. Figure 4 presents a comparison of the compressive strength of tested materials. The sample contained 0.5% of waste fibers was characterized by the highest compressive strength (46.3 MPa). The further increase in the content of the fibers caused a slight decrease in the compressive strength, which may be related to the deterioration of the workability and the problem of even distribution of the fibers in the matrix [17, 23-24]. In the case of the bending strength presented in figure 5, as the fiber content increased, the bending stress resistance also increased. However, the noticeable effect was achieved only when the fiber content exceeded 0.75% by weight.

![Figure 4. Comparison of compressive strength of tested materials](image1)

![Figure 5. Comparison of flexural strength of tested materials](image2)

The incorporation of fibers into geopolymer materials can also affect the wear rate. Fibers can act in many ways, ranging from reducing the degree of wear, limiting the propagation of cracks, to increasing the degree of wear, because if the fibers are pulled out of the matrix and additionally remain in the friction zone, they can act as an additional abrasive [25]. Table 3 presents a summary of the results obtained from the abrasion test for the manufactured composites. The results showed a similar resistance to wear, which is a favorable effect due to the type of applied fiber like tow.
The form of the fibers, such as pulp, makes it difficult to evenly distribute the fibers in the matrix of the composite and may contribute to a deterioration of the strength properties as well as the wear resistance because the fibers pulled out from the matrix are drawn as bundles of fibers which may result in greater loss of material. However, in this case, such behavior was not observed, which suggests a fairly good connection between the composite components. It may be related to quite good penetration of geopolymeric material between the fibers, which results in good bonding of the matrix material with the reinforcement.

4. Conclusions
The paper presents the possibility of using waste flax pulp. Strength tests revealed that the introduction of fibers in this form positively affects the mechanical properties. Introduction 1% by weight of fibers increased compressive and flexural strength above 10%. An interesting result was also noticed performing the abrasion resistance tests because no increase in the wear of such materials was seen, which is a positive behavior. These studies indicate the potential of using waste fibers as a process of their utilization. Additionally, this type of fibers may correctly fulfill the role of reinforcement in geopolymer composites. In summary, waste fibers show great potential and can be successfully used as reinforcement of geopolymeric materials.

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Table 3. Abrasive test results

| Index | Average height before the test (mm) | Average height after the examination (mm) | Average height loss (mm) |
|-------|-----------------------------------|-----------------------------------------|-------------------------|
| BM    | 71.2±0.5                          | 70.4±0.4                                | 0.9±0.02                |
| 0.25W | 71.2±0.7                          | 70.4±0.2                                | 0.8±0.03                |
| 0.5W  | 71.4±0.3                          | 70.6±0.5                                | 0.8±0.01                |
| 0.75W | 70.9±0.1                          | 70.2±0.2                                | 0.7±0.02                |
| 1W    | 71.5±0.2                          | 70.6±0.3                                | 0.9±0.01                |
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