Design and characterization of geopolymer foams reinforced with Miscanthus x giganteus fibers

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Abstract

This paper presents the effects of different amounts of fibers and foaming agent, as well as different fiber sizes, on the mechanical and thermal properties of fly ash-based geopolymer foams reinforced with Miscanthus x giganteus fibers. The mechanical properties of the geopolymer foams were measured through compressive strength, and their thermal properties were characterized by thermal conductivity and X-ray micro-computed tomography. Furthermore, design of experiment (DoE) were used to optimize the thermal conductivity and compressive strength of Miscanthus x giganteus reinforced geopolymer foams. In addition, the microstructure was studied using X-ray diffraction (XRD), Field emission scanning electron microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR). Mixtures with a low thermal conductivity of 0.056 W (m K)$^{-1}$ and a porosity of 79 vol% achieved a compressive strength of only 0.02 MPa. In comparison, mixtures with a thermal conductivity of 0.087 W (m K)$^{-1}$ and a porosity of 58 vol% achieved a compressive strength of 0.45 MPa.

1. Introduction

The demand for sustainable and ecological building and insulation materials is growing, especially due to the advancing climate change and the depletion of fossil resources. Thermal insulation materials are of particular interest for reducing the energy consumption of buildings. Currently, the most commonly used materials for thermal insulation include mineral wool, polystyrene, and polyurethane. However, the disadvantage of these products is their high global warming potential (GWP) compared to renewable materials. Thus, sustainable insulation materials based on renewable resources represents a possible alternative to conventional thermal insulation materials and is an essential step toward reducing CO$_2$ emissions. [1–4] Nowadays, bio-based materials like wood chips, cork, hemp, flax, and cellulose are mainly applied in thermal insulation [5].

Furthermore, fast-growing low-input grasses such as Miscanthus are a very promising group of renewable raw materials. Miscanthus is a perennual, rhizome-forming C4 grass and, due to its high parenchyma content and the associated good thermal insulation properties, of particular interest for use as insulation material. As a low-input plant, Miscanthus delivers high biomass yields with low nutrient inputs. Moreover, Miscanthus has, due to its C4 photosynthetic pathway, increased photosynthetic activity and can permanently capture 10 to 36 tons of CO$_2$ per hectare and year during growth. [5–9] Overall, there are appr. 17 species of the genus Miscanthus, the most common species in Europe are Miscanthus sinensis, Miscanthus sacchariflorus, Miscanthus floridulus, Miscanthus robustus and Miscanthus x giganteus [10–12]. According to Pude et al. Miscanthus x giganteus is the most suitable genotype for use in lightweight concrete. Their study investigates the suitability of different Miscanthus genotypes for the application in lightweight concrete to determine the influence factors on compressive strength. The highest values for the compressive strength were obtained for the lightweight concrete samples with the genotype Miscanthus x giganteus. Compared to the other investigated genotypes, Miscanthus x giganteus has a higher cellulose content, a thicker outer ring and exhibits the highest velocity and the maximum height of water movement. [11] Chen et al. investigated ultra-lightweight...
Miscanthus concrete (ULMC) for use as acoustic and thermal insulation. The ULMC with 30 vol% Miscanthus fibers achieves a thermal conductivity of 0.09 W (m K)\(^{-1}\) and a high acoustic absorption coefficient of 0.9 at low frequencies. Furthermore, their results show that the compressive strength is decreased, and the acoustic absorption and the thermal conductivity are increased by increasing the percentage of Miscanthus fibers. [13]

To reduce CO\(_2\) emissions, it is also necessary to find alternatives in the field of binders because the cement industry releases large quantities of CO\(_2\). The production of cement emits ~ 600 kg of CO\(_2\) per ton of cement. [14] One potential alternative to cement-based lightweight concrete is foamed geopolymers. Geopolymers are composed of an aluminosilicate source and an alkaline activator. Typical aluminosilicate sources are fly ash, metakaolin, or granulated blast-furnace slag. The alkaline activator is usually an alkali metal silicate or hydroxide. Foamed geopolymers can be produced by mechanical foaming, chemical foaming, or by forming a syntactic foam. [15–19]

For optimizing the properties of geopolymer foams, recent innovations have focused on fiber reinforcement [20–23]. Masi et al. investigated fly ash-based geopolymer foams reinforced with PVA (poly (vinyl alcohol)) and basalt fibers and chemically foamed with hydrogen peroxide. The samples with PVA fiber achieved a thermal conductivity of 0.30 W (m K)\(^{-1}\) and the samples with basalt fibers achieved a thermal conductivity of 0.38 W (m K)\(^{-1}\), while the not foamed geopolymers exhibited a thermal conductivity of 0.53 W (m K)\(^{-1}\). [20] Galzerano et al. studied lightweight geopolymers reinforced with hemp fiber grids. The metakaolin-based geopolymers were foamed by silicon metal powder and a mixture of vegetable surfactants. The chemical treatment of the hemp fiber grid due to the alkaline pH value of the geopolymer system leads to strong interfacial bonding between the geopolymer and the fibers, improving the mechanical properties. [23]

This study is based on the results from Walbrück et al. [22, 24]. These preliminary tests and previous studies have shown that the thermal conductivity and the compressive strength of Miscanthus fiber-reinforced geopolymer foams are influenced by the fiber size, fiber content and foaming agent content [22, 24]. Therefore, in this study the fiber content, fiber size and foaming agent content were varied to analyze their behavior on the thermal conductivity, porosity, compressive strength, composition, and microstructure of the Miscanthus fiber reinforced geopolymer foams. Furthermore, these parameters were varied to achieve an optimum mix design with low thermal conductivity and high compressive strength at the same time.

2. Materials und Methods

2.1 Materials

EFA-Füller HP (BauMineral, Germany) was used as fly ash for this study. The Miscanthus x giganteus fibers used in this study were cultivated at the field lab Campus Klein-Altendorf of the University of Bonn (Germany). Aqueous sodium silicate solution (SiO\(_2\) = 28.50 wt%, Na\(_2\)O = 8.29 wt%) purchased from Carl
Roth GmbH + Co. KG (Germany) was used as activator. Sodium dodecyl sulfate (SDS), from Carl Roth, was used as a foaming agent, while 1 wt% fumed silica nanoparticles Aerosil® 90 (Evonik Industries AG, Germany) were used to stabilize the foam.

2.2 Mix Design and Mixing Process

Design of experiment (DoE) was used to determine the optimal mixture with minimum thermal conductivity and maximum compressive strength. A full factorial design with three factors on two levels ($2^3$) and three replicates, plus one center point, were considered in the mix design. The center point is repeated nine times and thus a total of 33 experiments were performed. The nine experiments without their replicates are summarized in Table 1. The factors and their levels, as shown in Table 2, were chosen based on preliminary tests and previous studies [22, 24]. The preliminary tests and previous studies have shown that the thermal conductivity and the compressive strength of Miscanthus fiber-reinforced geopolymer foams are influenced by the fiber size, fiber content and foaming agent content [22, 24]. The results were evaluated by analysis of variances (ANOVA) and Pareto diagram using Minitab 18 (Minitab, Inc., USA).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fiber content [wt%]</th>
<th>Fiber size [µm]</th>
<th>Foaming agent content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>35</td>
<td>160</td>
<td>0.25</td>
</tr>
<tr>
<td>M2</td>
<td>35</td>
<td>160</td>
<td>0.35</td>
</tr>
<tr>
<td>M3</td>
<td>35</td>
<td>250</td>
<td>0.25</td>
</tr>
<tr>
<td>M4</td>
<td>35</td>
<td>250</td>
<td>0.35</td>
</tr>
<tr>
<td>M5 (Center Point)</td>
<td>40</td>
<td>200</td>
<td>0.30</td>
</tr>
<tr>
<td>M6</td>
<td>45</td>
<td>160</td>
<td>0.25</td>
</tr>
<tr>
<td>M7</td>
<td>45</td>
<td>160</td>
<td>0.35</td>
</tr>
<tr>
<td>M8</td>
<td>45</td>
<td>250</td>
<td>0.25</td>
</tr>
<tr>
<td>M9</td>
<td>45</td>
<td>250</td>
<td>0.35</td>
</tr>
</tbody>
</table>
The geopolymer foams were produced using the mixed-foaming method, in which the foam is generated during the mixing process by adding a surfactant to the slurry [15]. A dry mix of the solid components was activated by the alkaline solution (64 wt% sodium silicate and 36 wt% water) and mixed at high speed (speed position 2 of the mixer) for 5 min using a Hobart N50 mortar mixer. The mixture was poured into steel molds and cured at 50°C and ambient pressure for 48 h. Afterwards, the samples were demolded and cured at room temperature until 28 d.

2.3 Materials characterization

2.3.1 Thermal conductivity

The heat flow meter apparatus HFM 446 Lambda Small from Netzsch with two external thermocouples was used to determined the thermal conductivity of the foamed geopolymers (140x140x40 mm³). The two external thermocouples were placed on the front and back sides of the samples. The thermal conductivity of each mix design was measured on 3 samples with six measurements, respectively.

2.3.2 X-ray micro-computed tomography

The X-ray micro-computed tomography SkyScan 1275 from Bruker with a micro focus X-ray tube (100 kV and 100 µA) and a flat-panel detector was used to measure the porosity. The cylindrical samples (ø 20 mm) were scanned with a rotation step of 0.5 and a resolution of 14 µm over a 360° interval.

2.3.3 Compressive strength

The universal strength testing apparatus Z010 from Zwick/Roell was used for the compressive strength measurements. Samples with a size of 60x60x40 mm³ were measured at a testing speed of 2 mm min⁻¹ and an average of 3 samples for each mixture.

2.3.4 X-ray diffraction

A D2 Phaser X-ray diffractometer from Bruker AXS with a Cu Kα radiation source operating at 30 kV and 10 mA was used to identify the mineral phase composition of the geopolymer foams. The samples were measured with a step size of 0.01° and a scan time of 2.0 s step⁻¹ in the 2θ range of 10° to 65°. For the determination the crystalline and amorphous content via Rietveld refinement the samples were prepared by grinding and mixing 600 mg sample (< 63 µm) with 20 mg of the internal standard Lanthanum hexaboride (Sigma-Aldrich).

Table 2
Considered factors for the DoE.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Lower Level</th>
<th>Center Point</th>
<th>Higher Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber content [wt%]</td>
<td>35</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td>Fiber size [µm]</td>
<td>160</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>Foaming agent content [wt%]</td>
<td>0.25</td>
<td>0.30</td>
<td>0.35</td>
</tr>
</tbody>
</table>
2.3.5 Fourier-Transform Infrared Spectroscopy

The functional groups of foamed geopolymer concrete were determined using Fourier-Transform Infrared Spectroscopy (FTIR). The FTIR spectra were recorded on a FT/IR 410 spectrometer from Jasco between 450 and 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and 128 scans. The specimens were prepared by mixing 20 mg of sample in 1 g of potassium bromide (KBr).

2.3.6 Scanning electron microscope

The field emission scanning electron microscope JSM-7200 F from JEOL was used to investigated the microstructure of the foamed geopolymers. The SEM observations were carried out on small pieces of the samples mounted on a bulk sample holder.

3. Results and discussion

3.1 Compressive strength

Figure 1 shows the results of the compressive strength measurements. Sample M1 exhibits with 0.448 ± 0.052 MPa, the highest, and sample M9 with 0.020 ± 0.005 MPa, the lowest compressive strength (Table 3). The Pareto plot of the standardized effects in Fig. 2 compares the significance of each effect. In addition to the three factors, the 2-factor and 3-factor interactions were also considered. The significant factors exceed the orange reference line (\(\alpha = 0.05\)). For the response variable, compressive strength, the foaming agent content, fiber size and fiber content are significant, whereas no 2-factor or 3-factor interactions can be detected. The increased foaming agent content from 0.25 wt% to 0.35 wt% leads to a significant decrease in compressive strength. Furthermore, the increase of fiber size from 160 µm to 250 µm and the increased fiber content from 35 wt% to 45 wt% resulted, due to a less dense packing and a higher amount of parenchyma, in a decrease in compressive strength. Adding fibers can lead to both an increase and decrease in compressive strength. A decrease in compressive strength is observed when the increase in porosity overshadows the ability of the fibers to prevent cracks. If, on the other hand, the ability of the fibers to prevent cracks dominates, the compressive strength is increased. [25–27]
### 3.2 Thermal conductivity and porosity

Table 3 summarizes the thermal conductivity and porosity values of all geopolymer samples. Furthermore, Fig. 3 presents thermal conductivity results and Fig. 4 exhibit the Pareto diagram with the significant effects. For the response variable, thermal conductivity, fiber content, and foaming agent content are significant, whereas no effect of the fiber size and no 2-factor or 3-factor interactions are detected. The lowest thermal conductivity was achieved (0.056 W (m K)$^{-1}$) in the mixture M9 with 45 wt% Miscanthus fibers of the size 250 µm and with a foaming agent content of 0.35 wt%. A similar thermal conductivity (0.059 W (m K)$^{-1}$) was obtained in the mixture M7 with the same fiber content and foaming agent content and fiber size of 160 µm. An increase in fiber content and foaming agent content leads to a lower thermal conductivity and confirms the results of the previous study [22]. Furthermore, Fig. 5 presents the results of the porosity. The porosity is increased by increasing the foaming agent content. Sample M9, with the lowest thermal conductivity, also has the highest porosity.

### 3.3 X-ray diffraction

The XRD pattern of the geopolymer foam is shown in Fig. 6. The main components of the geopolymer foams are quartz (COD 9005020), mullite (COD 7105575) and hematite (COD 1011267) [22]. The mineralogical composition in Fig. 7 also exhibit that the geopolymer foams are about 60 wt% amorphous. The amorphous content is influenced by the fiber content. A higher fiber content leads to an increase in the amorphous phase. Sample M1 with a fiber content of 35 wt%, a fiber size of 160 µm and a foaming agent content of 0.25 wt% has an amorphous content of 56 wt%, whereas sample M6 (fiber content 45 wt%, fiber size 160 µm, foaming agent content 0.25 wt%) has an amorphous content of 58 wt%. However, sample M5, with a fiber content of 40 wt%, has a lower amorphous content than those
with a fiber content of 35 wt%. Compared with the samples with a fiber content of 45 wt%, the amorphous phase increases. Furthermore, the amorphous content decreases slightly with increasing foaming agent content. An increase of the foaming agent from 0.25 wt% to 0.35 wt% leads to a decrease in the amorphous phase from 56 wt% to 52 wt% for samples M1 and M2.

### 3.4 Fourier-Transform Infrared Spectroscopy

Figure 8 displays the IR spectra of the foamed geopolymer concretes and Table 4 summarizes the assignment of characteristic FTIR signals according to literature data [28–36]. The IR spectra exhibit main absorption bands at 3423, 2919, 2851, 1652, 1043, 776 and 488 cm$^{-1}$. The bands at ~3423 cm$^{-1}$ and ~1652 cm$^{-1}$ correspond to the O-H and H-O-H stretching and bending vibration, attributed to the weakly bonded water and to the O-H stretching from the cellulose and lignin structure of the Miscanthus fibers [28, 29, 37]. Moreover, the bands at ~2919 cm$^{-1}$ and ~2851 cm$^{-1}$ represent the stretching vibration of C-H, which is attributed to methyl and methylene groups and is related to the Miscanthus fibers [30]. The peak centered around ~1043 cm$^{-1}$ is assigned to the Si-O-T (T = Si or Al) asymmetric stretch of the tetrahedral SiO$_4$ or AlO$_4$ bonds and is characteristic of the geopolymerization [31–33]. Furthermore, the band at ~776 cm$^{-1}$ can be assigned to the Si-O-Si symmetric stretching vibration and is related to the presence of quartz [33–36]. The peak around ~488 cm$^{-1}$ arises due to the Si-O-Si asymmetric bending of SiO$_4$ tetrahedral [33, 34].

Comparing the FTIR spectra of the geopolymers in Fig. 8, there are no notable differences between the mixtures. Here, only the band of the asymmetric Si-O-T (T = Si or Al) stretching at 1043 cm$^{-1}$ should be mentioned. By increasing the foaming agent content, the bands shifting to lower wavenumbers. According to Wang et al. and Rees et al. the shift to lower wavenumbers is related to the incorporation of Si and Al into the geopolymer network. Especially, if more Al is incorporated into the network, the band shifts due to the lower binding strength of Al-O to lower wavenumbers. [36, 38] Thus the proportion of Si-O-Al to total Si-O-T is higher in sample M2 (1032 cm$^{-1}$) with 0.35 wt% foaming agent than in sample M1 (1054 cm$^{-1}$) with 0.25 wt% foaming agent.
Table 4

Characteristics of FTIR band for *Miscanthus* fiber-reinforced geopolymer foams [28–36].

<table>
<thead>
<tr>
<th>Wavenumber [cm⁻¹]</th>
<th>Functional group</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3423 ± 3</td>
<td>O-H, H-O-H</td>
<td>Stretching</td>
</tr>
<tr>
<td>2919 ± 2</td>
<td>C-H</td>
<td>Stretching</td>
</tr>
<tr>
<td>2851 ± 1</td>
<td>C-H</td>
<td>Stretching</td>
</tr>
<tr>
<td>1652 ± 1</td>
<td>H-O-H</td>
<td>Bending</td>
</tr>
<tr>
<td>1043 ± 12</td>
<td>Si-O-T (T = Si, Al)</td>
<td>Asymmetric Stretching</td>
</tr>
<tr>
<td>776 ± 2</td>
<td>Si-O-Si</td>
<td>Symmetric Stretching</td>
</tr>
<tr>
<td>488 ± 4</td>
<td>Si-O-Si</td>
<td>Asymmetric Bending</td>
</tr>
</tbody>
</table>

### 3.5 Scanning electron microscope

Figure 9 and 10 show the microstructure of mixture M1 and M9. Both SEM images reveal a porous structure, embedding fibers and unreacted fly ash particles in the geopolymer matrix. The geopolymer covers nearly the whole fiber surface, which indicates a good interaction between the fibers and the matrix. Furthermore, sample M9 exhibit between the fibers a honeycomb-like structure with lamellae widths of 7 to 19 µm. This supports the findings of the X-ray micro-computed tomography. When the volume of gas in the foam is more than 75%, the bubbles necessarily deform each other and and a polyhedral foam is formed. [39] Sample M9 exhibit a porosity of 79.2%, which indicates the formation of a polyhedral foam. In contrast, sample M1 has a porosity of 57.5% and also a denser structure can be observed on the SEM images. Furthermore, these results also support the results of the compressive strength and thermal conductivity. Sample M1 exhibit due to the denser structure a higher compressive strength and thermal conductivity compared to sample M9.

### 4. Conclusions

In this study, the fiber content, fiber size and foaming agent content were varied to analyze their behavior on the mechanical and thermal properties of fly-ash-based geopolymer foams reinforced with *Miscanthus x giganteus* fibers. The foaming agent content, fiber size and fiber content significantly affect the compressive strength, whereas no 2-factor or 3-factor interactions can be detected. The optimal conditions for maximum compressive strength are 35 wt% fibers with a fiber size of 160 µm and 0.25 wt% foaming agent. In contrast, only the fiber content and foaming agent content have a significant effect on thermal conductivity. The optimal conditions for minimal thermal conductivity are 45 wt% fibers and 0.35 wt% foaming agent. The SEM images exhibit that almost the whole fiber surface is covered by the geopolymer matrix. Furthermore, sample M9 with the lowest thermal conductivity exhibit a
honeycomb-like structure between the fibers. The FTIR results show an increase of the wavenumber corresponding to the Si-O-T (T = Si or Al) asymmetric stretching vibration by increasing the foaming agent. According to Ravikumar et al., the change to higher wavenumbers indicates a higher degree of polymerization [31].

**Declarations**

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**Author Contribution**

K.W.: Conceptualization, Investigation, Writing—Original draft preparation, Writing—Review and Editing, Visualization, Corresponding AuthorS.W: Writing—Review and Editing, Supervision, Project administration, Funding acquisitionD.S: Writing—Review and Editing, Supervision

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Figures
Figure 1

Compressive strength of Miscanthus fiber-reinforced geopolymer foams vs. fiber content wt% (A), fiber size µm (B) and foaming agent content wt% (C).
Figure 2

Pareto plot of the standardized effects for compressive strength ($\alpha = 0.05$).
Figure 3

Thermal conductivity of Miscanthus fiber-reinforced geopolymer foams vs. fiber content wt% (A), fiber size µm (B) and foaming agent content wt% (C).
Figure 4

Pareto plot of the standardized effects for thermal conductivity ($\alpha=0.05$).
Figure 5

Porosity of Miscanthus fiber-reinforced geopolymer foams determined by X-ray micro-computed tomography vs. fiber content wt% (A), fiber size µm (B) and foaming agent content wt% (C).
Figure 6

XRD Rietveld refinement for sample M1.
Figure 7

Mineralogical composition of the samples determined by Rietveld refinement.
Figure 8

FTIR spectra of Miscanthus fiber-reinforced geopolymer foams.
Figure 9

SEM image of sample M1.

Figure 10

SEM image of sample M9.