The influence of microstructure on mechanical properties of 3D printable geopolymer composites

Kinga Korniejenko^{1,*}, *Krzysztof Miernik*¹, *Wei-Ting Lin*², and *Arnaud Castel*³

¹Cracow University of Technology, Faculty of Material Engineering and Physics, Institute of Materials Engineering, Warszawska 24, 31-155 Cracow, Poland

²National Ilan University, Department of Civil Engineering, Shennong Rd., I-Lan 260, Taiwan

³University of Technology Sydney, School of Civil and Environmental Engineering, 81 Broadway, Ultimo NSW 2007, Sydney, Australia

Abstract. The additive manufacturing technologies are fast-developing industrial sector and, potentially, a ground-breaking technology. They have many advantages such as the saving of resources and energy efficiency. However, the full exploitation of 3D printing technology for ceramic materials is currently limited; a lot of research is being conducted in this area. A promising solution seems to be geopolymers, but its application requires a better understanding of the behaviour this group of materials. This article analyses the influence of microstructure on mechanical properties whilst taking the production method into consideration. The paper is based on comparative analysis – the investigation is focused on the influence of material structure on the mechanical properties and fracture mechanism of these kinds of composites, including those reinforced with different kind of fibres. As a raw material for the matrix, fly ash from the Skawina coal power plant (located in: Skawina, Lesser Poland, Poland) was used. The investigation was made by SEM analysis. The results show that the microstructural analysis did not sufficiently explain the underlying reasons for the observed differences in the mechanical properties of the composites.

1 Introduction

With respect to construction materials, additive technologies have been found to be the most viable option for widespread use in automated construction processes in the near future [1, 2]. They have many advantages such as resource saving, energy efficiency and friendliness towards the environment [3, 4]. However, the full exploitation of additive technology for effective application in the construction industry still requires optimisation, especially with regard to improving methods of designing new materials [5-7].

Some of the most promising materials for 3D printing technology in the construction industry are geopolymers [4, 7]. Nowadays, a lot of research works are conducted in this

* Corresponding author: kinga.korniejenko@pk.edu.pl

area, especially in the context of improving the key properties of additive manufacturing technology such as: short curing times, pumpability, printability and extrudability, buildability (the resistance of deposited wet material to deformation under loads), durability, ductility, vapour imperviousness, high tensile and compressive strength, low coefficient of thermal expansion, and resistance to UV light [4, 8, 9]. Unfortunately, its usage is limited, only some prototype elements have been performed using this technology [10, 11].

One of the possible ways to develop geopolymers for effective application in manufacturing on a larger scale is reinforcement of the material through the addition of fibres [6, 12]. Reinforcement in the case of geopolymers is highly required because of its brittle behaviour. The fibres improve ductility and limit crack propagation under tensile and flexural loading [8, 13]. The important task is to replace conventional steel bars (implemented to geopolymers from traditional concrete technology) with short fibres [3]. Hitherto, only a limited amount of research has been conducted in the area of fibre-reinforced 3D printable geopolymer composites, this includes:

- reinforcement with long steel fibres [14, 15] and short steel fibres [16];
- reinforcement with inorganic fibres, such as short glass fibres [17] and plastic fibres: PP, PVA and PBO [12, 18];
- reinforcement with natural fibres, i.e. flax [6, 7].

The main aim of this article is the investigation of the influence of material microstructure on the mechanical properties of the two kinds of composites (flax reinforced and carbon reinforced) and the comparison of two methods of production for geopolymer composites (casting and 3D printing).

2 Materials and methods

2.1 Materials

The geopolymer matrix was based on a fly ash and sand ratio of 1:1. The fly-ash came from the CHP plant in Skawina (Lesser Poland region, Poland). This fly ash has a chemical composition typical for class F [19, 20]. It contains up to 5% of unburned material, less than 10% of iron compounds and a low amount of calcium compounds. The amount of reactive silica in fly ash is around 36%. It also comprises a large amount of amorphous phase [19, 20]. The content of particles under the size of 45 μm is around 88% and the specific density of fly ash is 2.80 [19, 20]. These factors are important for the proper reactivity and good workability of this material during the geopolymerisation process. The specific density and fineness modulus of sand is 2.65 and 2.84, respectively [7].

As reinforcement, two kinds of fibres were used – green tow flax and carbon fibres (Fig. 1) – both at an amount of 1% by mass of the composites. Green tow flax fibres are by-products of textile fibre production – they are coarse, broken fibres, removed during flax processing. These fibres are of moderate stiffness and are usually shorter than 30 cm (Fig. 1a). The fibres used for this study were shortened to around 5 mm in length. The fibres were purchased from the Institute of Natural Fibres and Medicinal Plants in Poland. The properties of carbon fibres were not investigated in this study. The information given by the producer pointed to a density between 1.6 and 2.0 g/m^3 , a Young's modulus of 230 GPa, tensile strength in the range of 2800 - 5000 MPa and elongation of 1 - 1.5 %. They have a length of 5 mm and a diameter of 8 μm (Fig. 1b).

Fig. 1. The applied reinforcement: (a) green tow flax fibres [21], (b) carbon fibres.

2.2 Sample preparation

The samples were prepared using sodium promoter, fly ash, sand and fibres (1% by mass). The mass ratio of ash and sand was 1:1. Two kind of short fibres were applied – flax and carbon fibres.

The sodium promoter was made by mixing a sodium hydroxide solution (NaOH) combined with a sodium silicate (water glass) solution. To produce it, flakes of technical sodium hydroxide were applied to an aqueous solution of sodium silicate (R-145) for which the molar module was 2.50 and the density was about 1.45 g/cm^3 . For the process, tap water was used rather than distilled water. The alkaline solution was prepared by mixing the aqueous solution of sodium silicate with the solid sodium hydroxide. There were left until the concentrations equalised (around 2 hours). Next, the solid ingredients (fly ash, sand and fibres) were combined with the alkaline solution by using a low-speed mixing machine for around 10 minutes to obtain a homogeneous paste.

Two methods of production were then applied (Fig. 2):

- type “CAST”, in which traditional pouring molding was applied;
- type “3D”, in which samples were made by injection molding to simulate the 3D printing process.

Both types of samples (casted and injected) were heated in the laboratory drying cabinet for 24 h at 75°C . Afterwards, the samples were unoulded.

Fig. 2. The appearances of the samples made by the casting and injection methods.

The four series of the samples were prepared (Table 1).

Table 1. Information relating to the prepared samples.

Sample	Reinforcement	Production method
CASTC	1% carbon fibre	traditional moulding
CASTPZL	1% flax fibre	traditional moulding
3DC	1% carbon fibre	injection moulding to simulate 3D printing
3DPZL	1% flax fibre	injection moulding to simulate 3D printing

The samples were investigated with regard to their mechanical properties after 7 and 28 days [7]. A summary of these results is presented in Table 2 [7].

Table 2. The averages values for compressive and flexural strength after 28 days [7].

Sample	Flexural strength	Compressive strength
CASTC	8.3	43.9
CASTPZL	8.8	43.9
3DC	8.1	38.7
3DPZL	9.4	48.7

The unexpected finding in this research was the very high values of compressive and flexural strength of the composite with flax fibres in comparison with the composite with carbon fibres [7]. Next, the broken samples were stored in laboratory conditions for around 6 months. Microstructural research was then conducted.

2.3 Methods

A scanning electron microscope (SEM) of type JEOL JSM 5510LV was used for the microstructure research. Samples previously broken during compressive or flexural strength tests were used. The samples were mechanically crushed and covered with a thin layer of gold.

3 Results

SEM research was performed for all composites at different magnifications for the composites reinforced with fibres and for the different methods of production.

In Fig. 3, the microstructure of the cast samples reinforced with flax fibres is shown. On the left side, the structure of flax fibre is clearly visible. This is typical for natural fibre – the fibres are irregular due to their different dimensions and rough surface. The structure of the matrix is typical for fly ash-based geopolymers with aggregate [22-24]. The small holes left by unreacted spherical particles in the matrix are noticeable [25]. This is common for samples as revealed by investigating their mechanical properties. The matrix has also a very good cohesion with sand particles (right-hand picture).

The observed surface in Figs. 3-6 have a structure characteristic of the geopolymers after the curing process (min. 28 days) [26-28].

Fig. 3. Microstructure of the cast samples reinforced with flax fibres.

In Fig. 4, the microstructure of the injected samples reinforced with flax fibres is presented. There is no significant difference between the microstructure of the samples with flax fibres that were cast and those that were injected. The microstructure observation does not explain the significantly better results of compressive and flexural strength for the injected series of samples.

Fig. 4. Microstructure of the injected samples reinforced with flax fibres.

In Fig. 5, the microstructure of the cast samples reinforced with carbon fibres is depicted. In the microstructure, the agglomeration of the carbon fibres is presented. The investigation confirms the cohesion of the fibres and the geopolymer matrix (right picture). The structure of the matrix is similar to that of composites with flax fibres.

Fig. 5. Microstructure of the cast samples reinforced with carbon fibres.

In Fig. 5, the microstructure of the cast samples reinforced with carbon fibres is shown. The visible agglomeration of carbon fibres could have occurred due to worse mechanical

properties for this series of the samples; however, the visible agglomeration is also present for the cast samples and in this case, their occurrence did not result in a decrease of their mechanical properties. The matrix has the same structure as other series of composites.

Fig. 6. Microstructure of injected samples reinforced with carbon fibres.

For the chosen samples, the EDS analyses were conducted (Figs. 7 and 8 and Table 2).

Fig. 7. Microstructure for samples: a) CASTC, b) CASTPZL, c) 3DC, d) 3DPZL.

The EDS results are presented in Fig. 8. The charts are typical for geopolymers [27-29] The main element is silica due to the composition of raw materials – sand and fly ash. EDS analysis also shows a high content of oxygen, which is composed of oxides of various elements. A significant amount of aluminium is also observed. The high amount of aluminium and silica are necessary for a proper geopolymerisation process. The presence of sodium is also connected with the used promoter. Analysis also confirms a low ferrum and

calcium content. The composites also contain admixtures of other elements, e.g. small amounts of magnesium.

Fig. 8. EDS plots for samples: a) CASTC, b) CASTPZL, c) 3DC, d) 3DPZL.

Table 3 also shows the EDS analysis for the areas presented in Fig. 7 and the plots presented in Fig. 8.

Table 3. Results of EDS analysis (line: Ka).

Element	CASTC			CASTPZL			3DC			3DPZL		
	Intensity (c/s)	Atomic Conc.	Weight Conc.	Intensity (c/s)	Atomic Conc.	Weight Conc.	Intensity (c/s)	Atomic Conc.	Weight Conc.	Intensity (c/s)	Atomic Conc.	Weight Conc.
C	107.98	12.670	7.287	25.73	4.083	2.258	110.43	11.256	6.428	62.19	7.451	4.268
O	2,124.42	45.705	35.015	2,001.31	49.613	36.541	2,578.32	45.685	34.752	2,621.87	50.334	38.408
Na	985.74	5.767	6.348	866.50	6.033	6.385	1,094.55	5.046	5.516	1,087.08	6.046	6.629
Mg	125.07	0.549	0.639	89.49	0.470	0.526	178.60	0.612	0.708	78.37	0.330	0.382
Al	2,583.63	8.399	10.851	2,244.24	8.738	10.854	3,276.16	8.387	10.759	2,583.31	8.011	10.309
Si	6,965.09	22.464	30.211	6,871.03	26.687	34.504	9,761.54	25.008	33.394	7,944.72	24.354	32.623
K	530.87	1.401	2.624	467.12	1.522	2.739	542.82	1.171	2.178	458.28	1.175	2.190
Ca	556.74	1.479	2.838	481.89	1.575	2.906	775.57	1.677	3.196	483.35	1.241	2.372
Fe	414.17	1.566	4.187	277.85	1.279	3.287	376.84	1.156	3.070	290.63	1.058	2.818

The analysis did not confirm any significant differences for the elements between the composites produced by different methods. This finding does not explain the differences in

the mechanical properties. However, it must be noticed that the SEM test is quantity analysis, because it is made on small area.

4 Conclusions

Geopolymer composites based on fly ash reinforced with flax and carbon fibres were produced using two methods – casting and injection moulding (the latter being a simulation of the 3D printing process). The composites were prepared using a sodium promoter. The investigation of the samples was focused on the influence of the material structure on the mechanical properties of these kinds of composites.

The best values were achieved for composite reinforced by 1% flax fibre made by injection moulding to simulate 3D printing, and the worst were achieved for composite with 1% carbon fibre made by injection moulding to simulate 3D printing. The differences between mechanical properties for particular composition are statistically important.

The samples reinforced by flax fibres have similar fibre characteristics independent of the method of manufacturing. The microstructure observation does not explain the significantly better results of compressive and flexural strength for the injected series of samples. The composites with carbon fibres have an irregular distribution of fibres and both series show the cohesion of fibres with the matrix. The visible agglomeration of carbon fibres could cause worse mechanical properties for this series of the samples; however, the agglomeration is also visible for the cast samples and in this case, they did not result in a decrease of their mechanical properties. The matrix has the same structure as other series of composites.

The microstructural analysis does not sufficiently explain the underlying reasons for the observed differences in the mechanical properties of the composites. The microstructure observation did not show any significant differences between the matrices of the compositions. The EDS analysis does not show any significant differences between the analysed geopolymers.

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