Innovative Infrastructure Solutions (2024) 9:157
https://doi.org/10.1007/s41062-024-01469-7

TECHNICAL PAPER

Characterization of geopolymer composites for 3D printing: a microstructure approach

Passant Youssef[1] · Muhammad S. El-Feky[2] · Ahmed M. Ragab[3] · Mohamed I. Serag[3]

Received: 10 March 2024 / Accepted: 28 March 2024 / Published online: 24 April 2024

Abstract

Given the importance of geopolymer in terms of 3D printing performance and the scarcity of information on the subject, as well as previous research findings, the purpose of this study is to propose a design methodology for geopolymer concrete mix that can be used in the 3D printing process by studying the effect of fine aggregate size and type, binder type (either slag or metakaolin) and ratio (slag/metakaolin), and alkaline solution amount and ratio (NaOH/Na2SiO3). The study concluded that MK has lower fluidity than BFS under the same conditions that used the same amount of SP. However, it can be improved by adding slag. The best dosage was chosen, which is 50% MK and 50% BFS. Because of these proportions, the mixture is very dense, homogeneous and compact, which increases its microstructure analysis behavior.

Keywords 3D printing · Geopolymer · Metakaolin · SEM · TGA

Introduction

Many authors promote geopolymers as a "green" concrete solution; however, few studies [1, 2] have quantified the environmental impact of geopolymers using the Life Cycle Assessment method, including global warming, energy use and resource depletion. The most commonly used base binder materials in geopolymers are blast furnace slag (GBFS), fly ash (FA) and metakaolin (MK) [3, 4]. When used as waste from other industries, they have a lower environmental impact than cement [5]. It has been shown that the low Si/Al ratio of MK makes it necessary to use a lot of sodium silicate in the case of MK-based geopolymer concrete, which has a negative impact on the environment [6, 7]. While geopolymer concrete emits less CO_2 than OPC concrete [8, 9], this reduction is not enough to meet the environmental impact goals [10, 11]. In comparison, geopolymer concretes based on MK, FA and GBFS have less impact on the environment [12]. Contrarily, FA or GBFS has higher Si/Al molar ratios, allowing for a decrease in the use of sodium silicate [13, 14]. By combining MK and GBFS, Davidovits' solution was lowering its environmental impact because it contains less slag than a pure slag geopolymer and significantly less sodium silicate than a pure MK geopolymer [15].

The essential characteristics of effective 3D concrete printing are its new characteristics. The properties of substantial influence are not only the printability of the mixture but also the mechanical properties of concrete after setting. The rheology of the mixture influences the workability and extrudability of the concrete for smooth printing of layers with good shape stability, less void formation and a lower chance of nozzle blockage [16, 17]. Given the importance of geopolymer in terms of 3D printing performance and the scarcity of information on the subject, as well as previous research findings [18, 19], the current study objective is to study the effect of fine aggregate size and type, binder type (either GBFS or MK) and ratio (GBFS/MK), and alkaline solution amount and ratio (NaOH/Na2SiO3) on microstructure analysis of geopolymer composites according to the technical specifications of the 3D printing machine.

Reza et al. (2007) looked into how much high range water reducer would be produced if SF, MK and GBFS were used instead of OPC. Comparing the results to PC mixtures, it was found that using SF, MK and BFS instead of OPC increased HRWR demand. Due to its extremely fine nature

✉ Passant Youssef
passant.ahmed@guc.edu.eg

1 Civil Engineering Department, German University in Cairo, Cairo, Egypt

2 Civil Engineering Department, National Research Center, Cairo, Egypt

3 Civil Engineering Department, Cairo University, Cairo, Egypt

Table 1 Properties of slag (wt %)

Comp.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	SO_3	LOI
Const. (%)	42.07	0.74	10.26	1.79	3.73	5.6	31.15	0.5	0.63	0.03	0.15	2.88	0

and high surface area, SF is likely to have a high HRWR demand, whereas MK may have a low HRWR demand due to its stable structure, elongated shape and high surface area. The HRWR demand was lower in all BFS mixtures than in non-BFS-containing mixtures. Because of the morphology of the glassy slag particles and their smooth surface, BFS has a low adsorption potential. No matter the w/b ratio, the variation of HRWR with the binder material exhibited the same behavior [20]. Panda et al. (2018) revealed a geopolymer mortar material design created for 3D printing concrete using fly ash, silica fume, slag and sand with a particle size of 2 mm. According to the study, high sand ratios (1.7 and 1.9) led to material segregation and clogging because of high yield stress, which led to complex extrusion, slump and the material failed to withstand 60 layers. It was recommended to use a sand-to-binder ratio of 1:5. The material gradually became harder over time by lengthening the time between layers, which led to issues with pumping and pipe flow discontinuity [21]. A. Kashani et al. (2018) investigated the fresh properties of geopolymer mixtures to find an effective mixture that is 3D printing compatible. The study concluded that the activator and water-to-solid ratio influenced the mix properties. The best mix contained an 8% activator and a water-to-solid ratio of 0.33. Higher w/s ratios with low activator amounts caused particle separation and decreased shape stability. Higher activator concentrations resulted faster reaction, nozzle blockage and less adhesion between layers [22].

Experimental program

Materials

Grinded ground-granulated blast furnace slag is to be used naturally. Table 1 shows the chemical composition.

Sodium silicate is known commercially as "liquid glass" or "water glass." Depending on the desired application, sodium silicate products are manufactured as solids or thick liquids. Sodium hydroxide is a white solid in flakes, pellets, granular and solution forms. It is highly soluble in water. Table 2 shows the chemical composition of sodium silicate and sodium hydroxide used in this study.

To ensure that durable composites are produced, natural clear sand size 1.18 mm and quartz (600 µm) used in mortars are free of alkali-reactive materials. The water used in the mix design is potable water from the water supply network system free of suspended solids and organic materials

Table 2 Chemical composition of sodium silicate and sodium hydroxide

Chem. comp.	Sodium silicate (%)	Sodium hydroxide (%)
Na_2O	12	60.25
SiO_3	31	0
Water	57	39.75

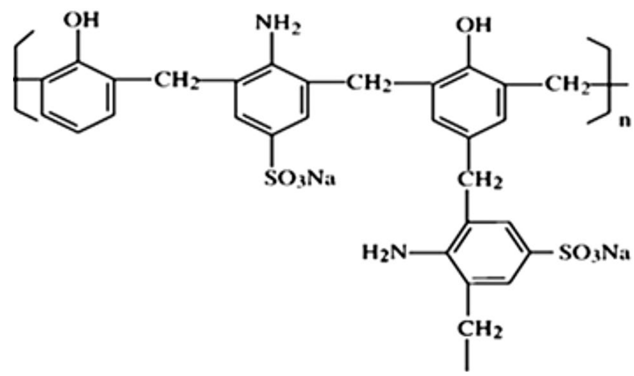

Fig. 1 Chemical composition of PFS

that can affect the properties of fresh and hardened concrete. PFS (phenol formaldehyde sulfonate) is a superplasticizer synthesized in a laboratory. Figure 1 depicts the chemical structures of the based materials synthesizing this admixture.

Samples preparation

The previous study [23] sought to provide guidelines for investigating the fresh and hardened properties of geopolymer mixtures to identify an effective mixture compatible with 3D printing technology. Twenty-four geopolymer mixtures were tested. The cement in these mixtures was replaced with GGBFS and MK (100% slag, 50% slag and 50% MK, 100% MK) and activated with sodium silicate and sodium hydroxide using 8% Na2O. The impact of several superplasticizer doses (0%, 0.25%, 0.5% and 0.75%) on binder material weight, activator ratio (NaOH/Na2SiO3=1:3) and water/binder ratio 0.33 was examined. A total of 144 mortar cubes (50*50*50 mm) were produced to perform the compressive strength test at 7 and 28 days according to ASTM C39, and 72 prisms (40*40*160 mm) were prepared to do the flexure strength test at 28 days according to ASTM C78. The current study investigated microstructure analysis based on SEM and TGA results at the age of 28 days for all samples. Various parameters are investigated to accomplish this, including the sand-to-MK ratio, sand size, superplasticizer dosage and activator ratio. The sample preparation will be divided into three groups. The 1st group consisted of eight mixes (A1 to B8) made by 100% slag as a binder material. The superplasticizer content was (0%, 0.25%, 0.5% and 0.75%) by binder weight, the water–cement ratio was 0.33, the sand-to-binder ratio was 1.5, and the sand size was 1.18 mm for the first 4 mixes and 600 µm for the rest. The second group (C9 to D16) included the same number of mixes by combining slag and MK in a 50:50 ratio, and the third group (E17 to F24) included mixes made entirely of MK (Table 3).

Results and discussion

Previous research [23] discovered that MK has lower fluidity than GBFS under the same conditions that used the same amount of SP. According to previous findings, 50% MK and 50% GBFS are the best dosages; the mix was very dense, homogeneous and compact, which increases its mechanical strength. The appearance of some cracks prior to total failure was observed in samples with 100% MK; this indicates that the material was fragile [24].

Scanning electron microscope

Figures 2, 3, 4 and 5 show SEM images of geopolymer samples prepared with 8% sodium hydroxide solution. The images show that the crystalline phases are transparent and well-formed in the MK and slag images. However, there are still unreacted silica particles in the structure of the 50 slag/50 MK samples, particularly in the mixes B5, D13 and F21. Mix D14 showed denser surface with less voids and pores. This indicates that the use of superplasticizer has a great impact on reducing pores; in addition, the SEM images showed a decrease in the voids and gaps size which has a good effect on improving the mechanical properties when compared to the mixes without the superplasticizer. It can be noticed that the hydration products indicate more impurities and pores in the case of mixes without the presence of the superplasticizer which consequently led us to the indication of the weakness in the samples and the lack of bonding and cohesion. This observation complies well with the lower compressive strength values of these mixes as previously mentioned [23].

Table 3 Constituents of geopolymer samples

Group	Mix	Slag (%)	MK (%)	Sand/slag	Water/binder	S.P. (%)	Act. (%)	NaOH/Na2SiO3
A	1	100	0	1.5	0.33	0	8	1:03
	2			Size 1.18 mm		0.25		
	3					0.5		
	4					0.75		
B	5			1.5		0		
	6			Size 600 µm		0.25		
	7					0.5		
	8					0.75		
C	9	50	50	1.5		0		
	10			Size 1.18 mm		0.25		
	11					0.5		
	12					0.75		
D	13			1.5		0		
	14			Size 600 µm		0.25		
	15					0.5		
	16					0.75		
E	17	0	100	1.5		0		
	18			Size 1.18 mm		0.25		
	19					0.5		
	20					0.75		
F	21			1.5		0		
	22			Size 600 µm		0.25		
	23					0.5		
	24					0.75		

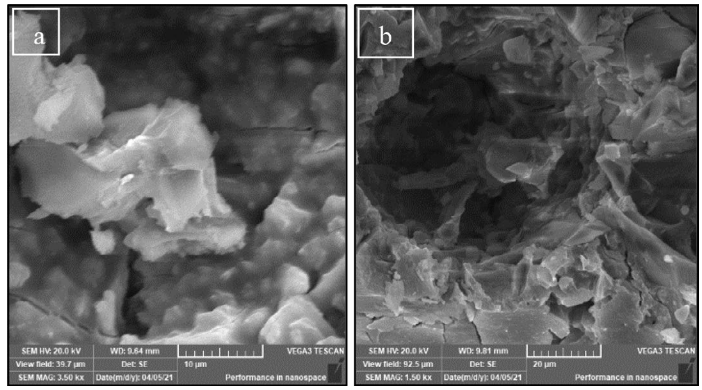

Fig. 2 SEM of mix B5, 10 µm (**a**), 20 µm (**b**)

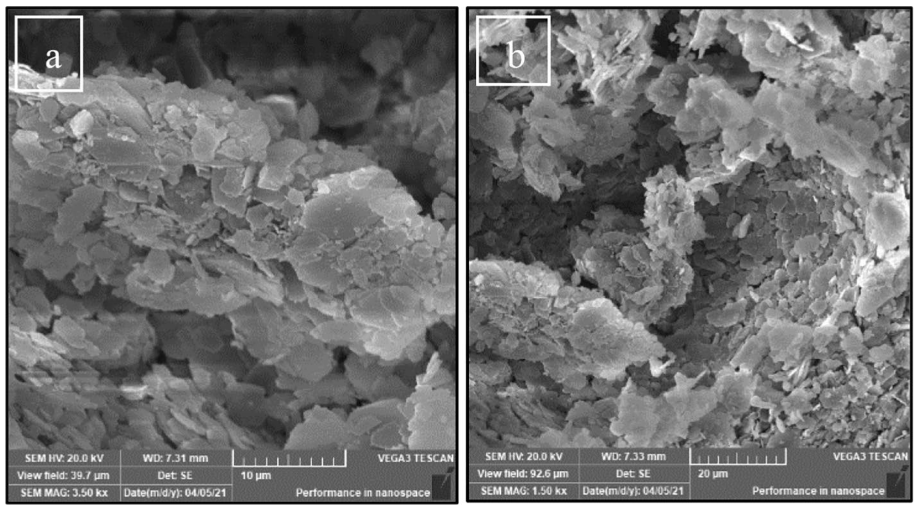

Fig. 3 SEM of mix F21, 10 µm (**a**), 20 µm (**b**)

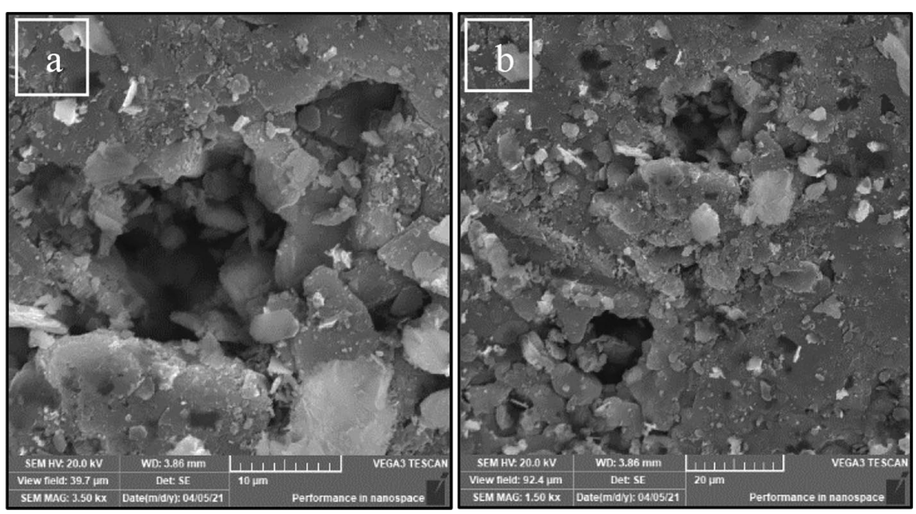

Fig. 4 SEM of mix D13, 10 µm (**a**), 20 µm (**b**)

Thermogravimetric analysis

The simultaneous TGA/DTA/DSC apparatus was used for thermal analysis. A nitrogen atmosphere with a 100 mL/min flow rate and a 10 °C/min heating rate was used. The powder samples were dried on the surface before the experiments by placing them in a glass beaker at 60 °C for 24 hours. The tests were carried out at room temperature (22 °C) and then elevated to 1000 °C using a platinum pan to avoid reacting with the material. The test results

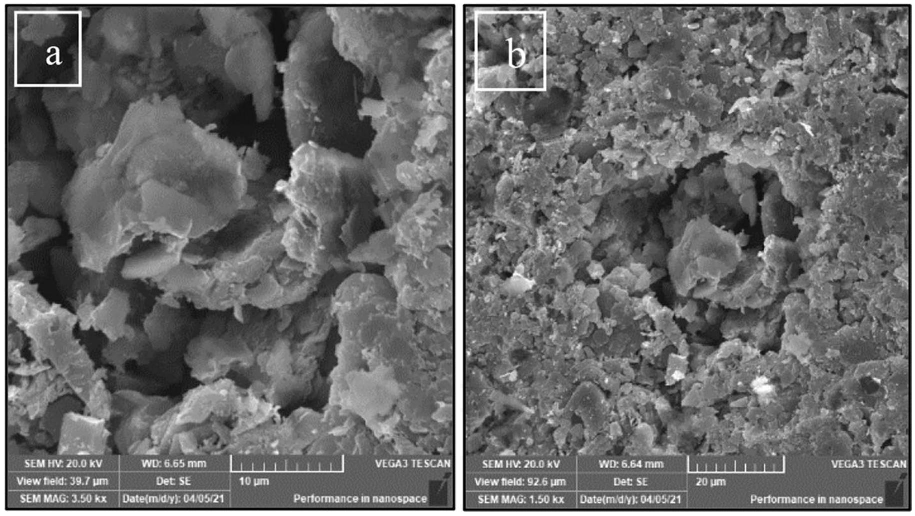

Fig. 5 SEM of optimum mix D14, 10 µm (**a**), 20 µm (**b**)

were analyzed using the TA Instruments Universal Analysis 2000 application. TGA analyses of the mixtures B5, F21, D13 and D14 are shown in Figures 6, 7, 8 and 9. At 1000 °C, mass loss varied from 6 to 9% depending on the composition of the mixture when milled slag compositions were compared to the three mixes without superplasticizer, GBFS, MK or 50/50 GBFS/MK-based geopolymer composites, and a more significant mass loss was observed, due to the formation of more geopolymer gel. On the other hand, the weight loss for a mix containing only MK is the smallest, followed by the weight loss for a 50/50 GBFS-MK-based geopolymer composite. TGA curves, like geopolymer composites, can be classified into four zones based on the data in the figures. Weight loss below 100 °C (area 1) is attributed to hygroscopic water evaporation, while weight loss between 100 and 300 °C (region 2) is attributed to structural water evaporation from the geopolymer gel [25–27]. Mass loss was approximately 1% in Region I and 1.5–3.5% in Region II. The removal of structural water caused by the condensation of silanol and aluminol groups in the geopolymer gel, generating Si–O–T tetrahedral links (T = Si or Al), is attributed to the continuous weight reduction observed between 300 and 800 °C (region III) [18, 25]. Mass loss in area III ranged between

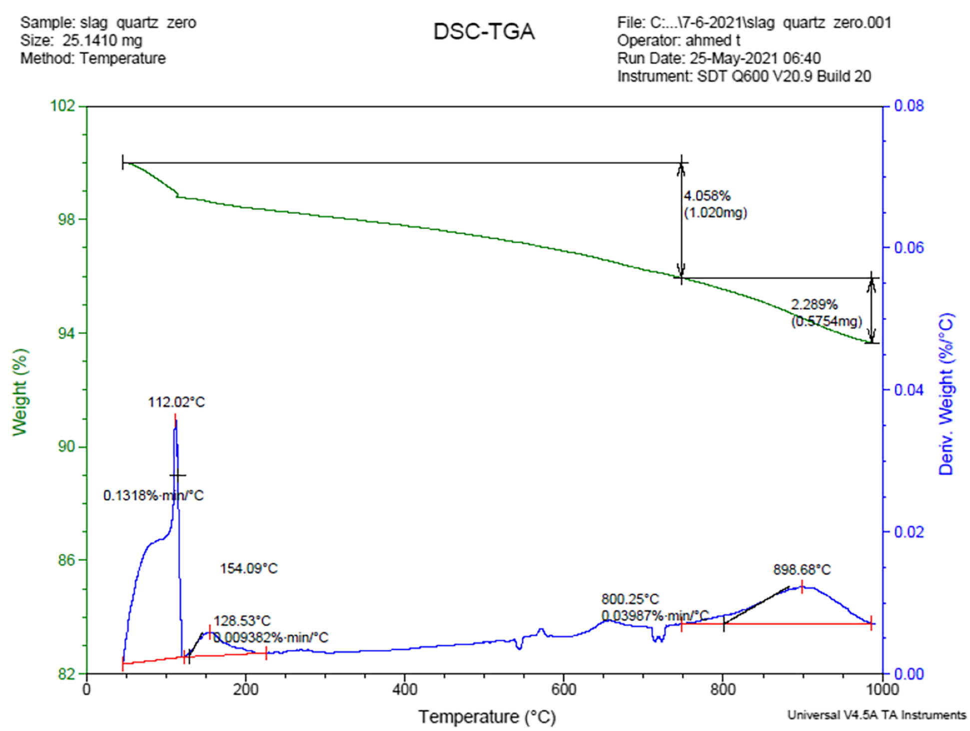

Fig. 6 TGA of mix B5

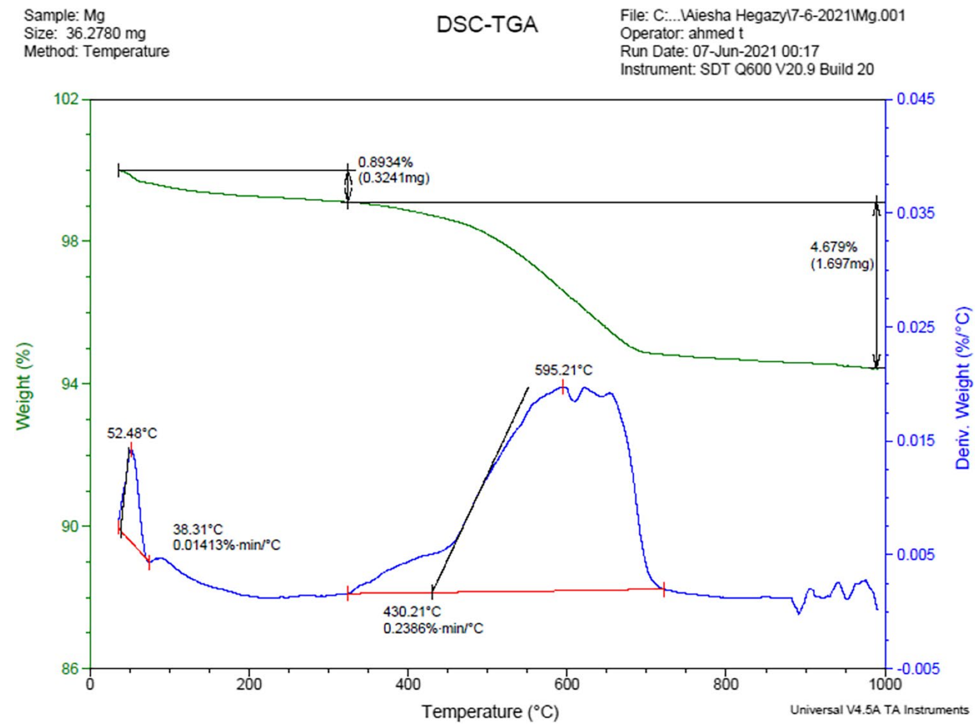

Fig. 7 TGA of mix F21

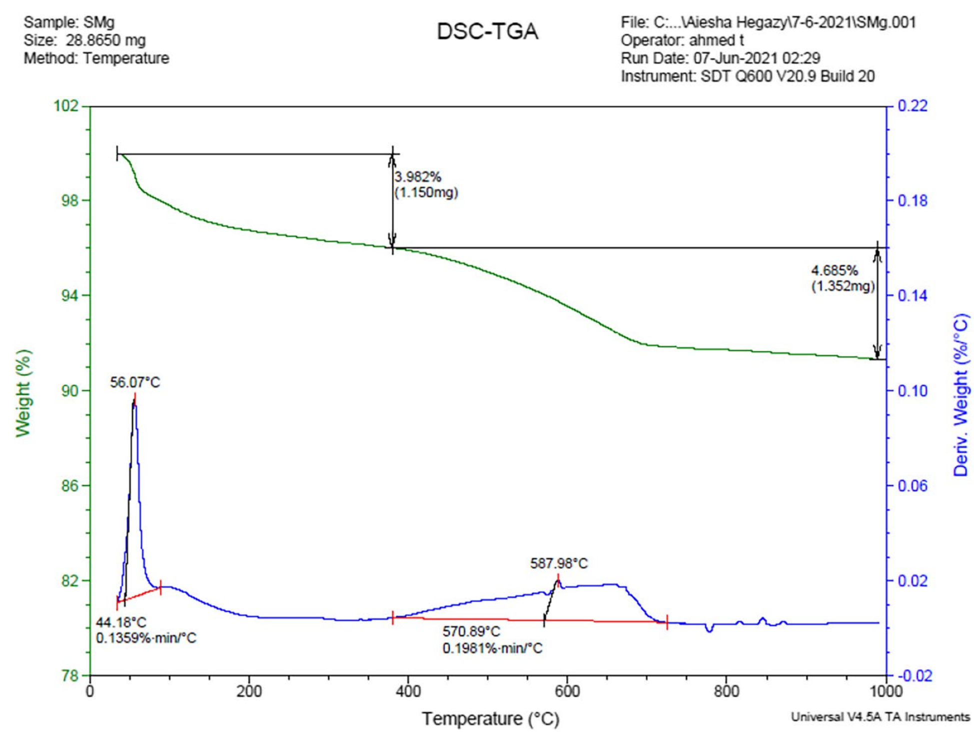

Fig. 8 TGA of mix D13

1 and 2%. No significant weight loss was observed above 800 °C (area IV), indicating the absence of additional thermal breakdown processes; above this temperature, sintering reactions begin, forming a ceramic body [27]. The mass retention of the produced geopolymers ranged between 93 and 96% at 1000 °C, indicating their comparatively high thermal stability. The weight loss was slightly lower when the superplasticizer was added than when the same mix without the superplasticizer. This could be attributed to the effect of the superplasticizer composition,

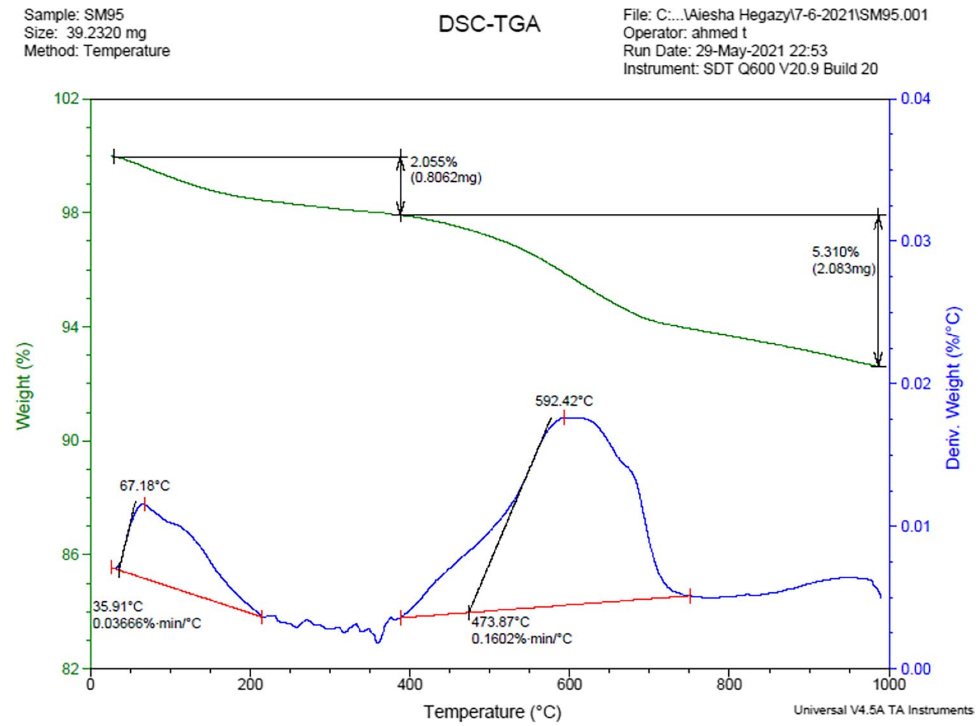

Fig. 9 TGA of optimum mix D14

which prevented the mix from carbonating. As a result, the calcium carbonate content of the mix decreased, as did the weight loss.

Conclusion

The study concluded that the BFS is amorphous and contains 31% lime (CaO) and 42% silica (SiO2). A large amount of sodium silicate was required due to MK's low Si/Al ratio, which has a significant environmental impact. Because of the cost savings associated with using less slag, mixing MK with slag is the optimum case. In comparison to pure MK-based geopolymer, less sodium silicate was required. Because it contains less BFS than a pure BFS geopolymer and much less sodium silicate solution than a pure MK geopolymer, a combination of MK and BFS was used to reduce environmental effects. In TGA, The weight loss was slightly lower when the superplasticizer was added than when the same mix composition was used without the superplasticizer due to the effect of the superplasticizer composition, which prevented the mix from carbonating. The calcium carbonate content of the mix decreased, as did the weight loss.

Author contributions All authors contributed to the study conception and design.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB).

Data availability The data that support the findings of this study are available on request from the corresponding author.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent Informed consent was obtained from all individual participants in the study.

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