

3D printing using metakaolin-based geopolymers - challenges

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Abstract

Alternative cementitious materials able to partially replace or supplement the use of Portland cement, such as geopolymers, are becoming increasingly attractive due to lower emissions of air pollutants during their production. In addition, coupling geopolymers with additive manufacturing technologies such as 3D printing can contribute to achieving some of the Sustainable Development Goals (SDG) of settling housing issues. Additive manufacturing allows producing pre-fabricated building elements or even entire houses. However, enabling 3D printing using geopolymers requires understanding concepts of rheology, technology, and material sciences, such as different possibilities of formulations, rheological behavior, printing parameters, curing methods, reinforcement content, and fiber type. Cylindrical specimens were printed both with and without polypropylene fibers by controlling the geopolymer matrix formulation, printer displacement speed, mass percentage of fibers, and material flow through the printer's extruder nozzle.

Keywords: geopolymerization, polypropylene fibers, 3D printer, additive manufacturing, rheology.

INTRODUCTION

There has been rising concern over climate change due to an increased concentration of carbon dioxide (CO₂) in the atmosphere, largely driven by such an enormous demand for Portland cement in construction industries [1-3]. Geopolymers are more ecological materials obtained by alkaline activation of aluminosilicates derived from natural minerals or industrial waste containing high levels of silica (SiO₂) and alumina (Al₂O₃) [4-6]. Given this, alternative cementitious materials e.g., geopolymers, are gaining soaring expressiveness in the scientific community, given that their production yields lower environmental harms, in addition to reaching over 70% global warming weakening potential depending on their formulation [7]. Hence, such novel materials are alternatives well capable of reaching some Sustainable Development Goals (SDG) related to technological and sustainable civil construction [8, 9], aside from the possibility of total or partial replacement of Portland cement on additive manufacturing [10, 11]. Coupling additive manufacturing with the construction sector holds promise in reducing construction project timelines and residues while at the same time enhancing safety tactics. Furthermore, it enables the production of diverse geometries in addition to those achievable through traditional molding methods [12, 13].

3D printing with Portland cement has already been used to build entire houses, offices, bridges, and lodges [14]. Nonetheless, using geopolymer instead proves the feasibility and emphasizes the relevance of investigating such a remarkable technology, since there should be an in-

depth understanding of its formulation which directly affects the assessment of the material rheological behavior, i.e. the paste's ability to flow under shearing stress and elevated yield stress when flow ceases, in which layer over layer is held without autoflowing. The complexities in finding proper rheology for printing lie in the geopolymer sensitivity to the kind of alkaline activator, the number of alkaline solution constituents, water and fiber percentage, aluminosilicate particle size, and plasticizing additives [10]. For instance, with regard to the chemical composition of precursors, it was observed that materials containing calcium oxide (CaO), such as blast furnace slag, can accelerate geopolymerization processes, thereby reducing material workability and leading to premature curing, in addition to hindering proper flow [10, 11]. However, if metakaolin were used as the precursor, there would be an increase in viscosity compared to blast furnace slag attributed to particle size distribution and morphology and characterized by angular or irregular shapes [11, 15]. Concerning the alkaline solution, molarity directly affects curing time and results in lower concentrations, i.e. the higher the water content, the longer the geopolymer paste remains fresh [15]. Nonetheless, if sodium hydroxide and sodium silicate were used separately, there would be a longer curing time, as opposed to what is observed while combining NaOH and Na₂SiO₃. In such a case, using a combined alkaline solution, regardless of the fact that the geopolymer cured faster, allowed for improvement in the mechanical properties of printed specimens, as well as their flowing ability and the fresh paste capacity of bearing upper layers [16]. Furthermore, it is observed that rheological behavior is also affected by the SiO₂ and Na₂O molar ratio, i.e. the higher it is, the better the extrusion process becomes [14, 16].

Additionally, apart from rheology and paste formulation, it is worth mentioning other aspects of extrusion-based additive manufacturing of geopolymers,

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such as printing parameters set on the slicer software, such as pumping pressure on the paste in the hose, amount of paste flowing through the nozzle, and product geometry, since these may lead to additional shearing stresses [10]. Furthermore, an elevated alkalinity of geopolymers could be harmful to the printer parts [16]. In addition to layer-by-layer deposition, achieving consistent printing requires controlling displacement velocity at the extrusion nozzle and ensuring precise leveling of the distance between the nozzle outlet and the printing surface. For such a purpose, the nozzle should not be too close to the print bed while printing initial layers so as to ensure no additional stresses, not to mention the fact that speed must be reduced. After the initial three-layer deposition, printing progresses at a higher speed and lower layer height until completion [17]. Geopolymers require an ideal extrusion nozzle displacement of 50 mm/s, as excessively high printing speeds result in reduced layer thickness, then potentially weakening layer adhesion [18]. Another challenge to be faced for successful 3D printing using geopolymers is the mechanical behavior of the material after curing, depending on printing patterns. A parallel lines pattern printed specimen exhibited less compression strength when compared to the one printed using a cross lines pattern. On the other hand, the flexure strength was higher when using a parallel lines pattern, compared to the sample printed using the cross-line pattern [19]. Furthermore, the fiber's average length must be longer than the nozzle outlet diameter to ensure flowability using thoroughly aligned reinforcements so as to allow controlling fiber alignment of the final product [19].

In light of the above, the present research aims to properly formulate a metakaolin-based geopolymer to be printed both with and without polypropylene fibers.

EXPERIMENTAL

Two different batches of metakaolin (HP Ultra, Metacaulim do Brasil) were used. Materials were analyzed regarding their chemical composition by X-ray fluorescence spectroscopy (XRF, Zetium, Malvern Panalytical), and particle size distribution was measured by laser granulometry technique (Mastersizer 3000, Malvern Panalytical). Other necessary materials were used such as sodium hydroxide (NaOH, Dinâmica Quím. Contemp.) provided in microbeads at 98% purity and sodium silicate (Na_2SiO_3 , Diatom Miner.) as an aqueous solution whose weight percentage composition was 29.7% of SiO_2 , 8.9% of Na_2O , and 61.4% of H_2O . Hydroxypropylmethylcellulose (HPMC, Aditex) was selected as a plasticizing additive having a specific mass of 0.425 g/cm³. The used surfactant additive was polyether carboxylate (ADVA-175, GCP Appl. Technol.) with a specific mass of 1.085 g/cm³, pH 6.5, and <150 cps viscosity. Polypropylene (PP, Saint-Gobain) fibers with 9 mm in length and 12 μm in diameter were used. Formulation parameters for the geopolymer prepared using metakaolin from batch 1 are shown in Table I.

Table I - Parameters of geopolymer formulation using metakaolin from batches 1 and 2.

Parameter	Batch 1	Batch 2
Molar ratio Si/Al	3.00	5.75
Mass ratio $\text{Na}_2\text{SiO}_3/\text{NaOH}$	2.00	0.85
Alkaline solution molarity (mol/L)	5.0	7.5
Mass ratio of alkaline solution/ metakaolin	0.805	0.604
Water content (wt%)	29.4	21.8

Plasticizer and surfactant contents were initially set at 2% of metakaolin weight and 1.5% of total weight, respectively. PP fiber content was initially fixed at 0.25% of total weight. The alkaline activator preparation was initiated by sodium hydroxide dissolution in distilled water, which was mixed with the sodium silicate solution afterward. The solution was left idle until it was thoroughly cooled for 24 h, while the weighing of solid materials took place, starting from metakaolin, followed by HPMC and then the fibers that had been totally unraveled by hand before mixing so as to avoid the formation of agglomerates. Then, the last component, the polyether carboxylate (ADVA-175) was weighed. Geopolymer preparation started out by mixing metakaolin with HPMC for 5 min in a benchtop planetary mixer (400040-60, EngeTotus). Next, an alkaline solution was added to the recipient containing the metakaolin and plasticizer. After a few seconds, when the powder began to agglomerate, the surfactant was added. The mixing process lasted 20 min. The same procedure was carried out while preparing geopolymer by slowly adding PP fibers whilst the metakaolin and plasticizer were mixed before alkali and surfactant activation. After paste preparation and before the printing process, it was used an adapted 3D printer (Duraprinter E02, Duracer). The printer's pneumatic reservoir internal surface was covered with an anti-seize oil, as well as the extrusion head and the hose.

A 35 mm diameter x 70 mm height cylinder was designed as a test specimen on AutoCAD 3D and saved as 'stl' to be sliced on a slicer software (Ultimaker Cura) so that it was sent to the printer. Printing parameters were selected considering the diameter of 1.55 mm of the extruder nozzle, 1.40 mm of layer thickness for the five initial layers, and 1.00 mm of height for the ones remaining. It is worth mentioning that layer thickness was the same as the extruder outlet diameter, with head displacement at 50 mm/s for the initial layers, followed by 65 mm/s until printing was finished. A brim was added by selecting this option on the software in order to ensure a non-spreading of the cylinder base while printing. Material flow was set at 80% for the brim, 100% for the five initial layers, and 120% for all the subsequent ones. The printing patterns used were the parallel lines and cross-lines type. After all these settings, a 'gcode' file format was generated and saved on the printer's memory card. Then, the printer pneumatic reservoir was rapidly filled with the obtained geopolymer, and the hose was attached to it right after paste preparation. The pressure was set at 10 bar, thereby commencing the printing procedure.

RESULTS AND DISCUSSION

The chemical composition and particle size distribution results from each metakaolin batch are shown in Table II and Fig. 1.

Table II - Chemical composition (wt%) by XRF analysis of metakaolin from batches 1 and 2.

Oxide	Batch 1	Batch 2
SiO ₂	48.36	69.50
CaO	0.57	0.10
Al ₂ O ₃	36.68	24.10
Fe ₂ O ₃	5.32	2.10
MgO	0.86	0.28
P ₂ O ₅	-	<0.10
Na ₂ O	-	<0.10
K ₂ O	6.21	0.39
MnO	-	<0.10
TiO ₂	2.78	1.68

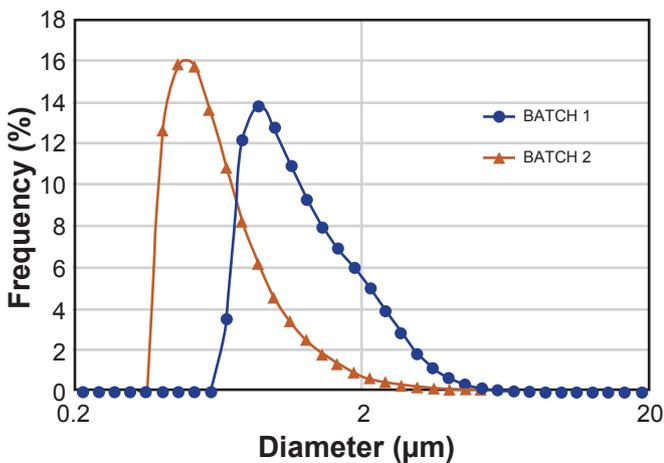


Figure 1: Particle size distribution curves for both metakaolin batches.

During the first printing test on the geopolymer prepared using metakaolin from batch 1, the original pneumatic reservoir constructed with an aluminum alloy suffered from corrosion due to high alkalinity [16]. The chemically affected internal cylinder wall is shown in Fig. 2, which became rougher and caused piston locking. A new pneumatic reservoir was manufactured in accordance with ISO 6431 standard aiming to ensure a continuation of experimental tests, but by incorporating an AISI 304 stainless steel cylinder instead of an aluminum alloy one, in addition to a piston and an outlet cap made of SAE 1020 steel (Fig. 3).

Once the new reservoir was in place, the geopolymer was prepared using metakaolin from batch 1. An alkaline solution at 5 M molarity was used and the paste presented excellent capacity for manual molding, probably due to the high pH caused by the presence of calcium oxide combined with sodium silicate and sodium hydroxide [16]. However,



Figure 2: Image of aluminum pneumatic reservoir chemically affected by the geopolymer.

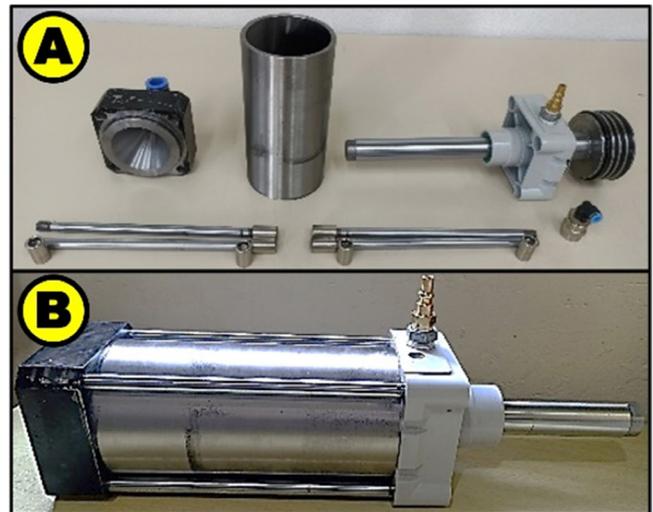


Figure 3: Images of the pneumatic reservoir with a stainless-steel cylinder disassembled (a) and assembled (b).

the geopolymer paste did not flow despite the fact that the system pressure was set at 10 bar. This was possibly due to the fact that the paste's initial yield stress was greater than the printer's capacity. Therefore, it was opted to reduce the alkaline solution molarity to 4.5 M using a higher volume of water than in the previous test [15, 16]. Still using the metakaolin batch 1, a new geopolymer paste was prepared and submitted to another printing test. A lower molar concentration allowed better manual molding and enhanced rheology to be used in the 3D printer system. Nevertheless, the paste showed no stability and collapsed under its own weight only after 10 layers, which was spread on the printing area and could reveal a possible overmeasure of water. Moreover, the outlet flow exhibited some discontinuities. Thus, an intermediate alkaline solution molarity of 4.75 M was chosen and the extrusion head displacement was reduced from 65 to 50 mm/s for all layers. Given these parameters, another geopolymer paste was prepared using

metakaolin from batch 1, resulting in a complete sample printed with uniform dimensional accuracy regarding the external diameter and layer height (Fig. 4).

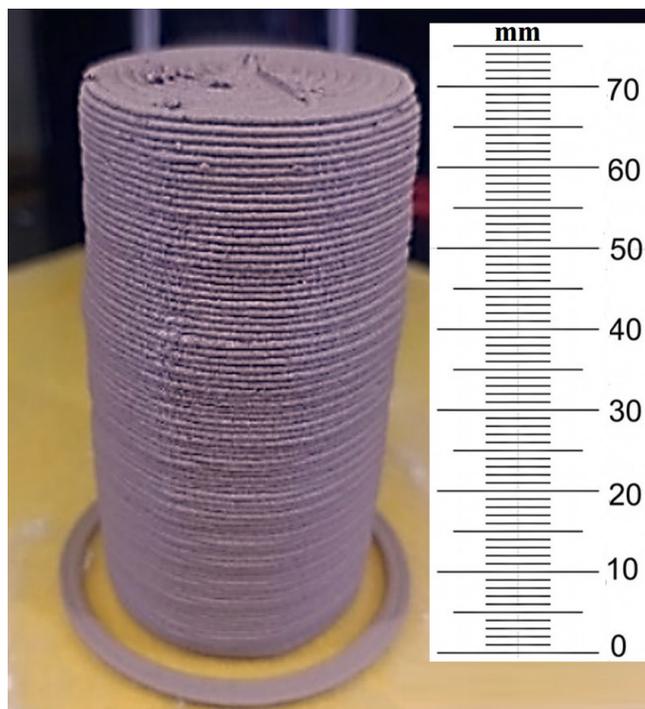


Figure 4: Image of cylindric geopolymer sample printed using metakaolin from batch 1 and a 4.75 M alkaline solution.

Metakaolin from batch 2 was used as follows. An attempt to reproduce the same formulation for the geopolymer paste was made, but the resulting material showed a totally self-compacting behavior, which is unsuitable for a 3D printing process. It is worth mentioning that metakaolin from batch 2 had both different chemical composition and particle size distribution from batch 1 (Table II and Fig. 1). Therefore, after some qualitative tests on metakaolin from batch 2, a new paste was formulated and it had similar rheological behavior to the one obtained from batch 1. The new formulation parameters are listed in Table I. It is also worth mentioning that there was a significant change in the mass ratio between sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) by comparing geopolymer formulations prepared from different batches of metakaolin. Initially, it was 2, but the new value was found as 0.85. This could reveal the rheological dependence on the physical and chemical characteristics of geopolymer formulation, such as particle size distribution and morphology, and chemical composition [10, 11, 14-16]. For instance, both metakaolin batches presented different Al_2O_3 and SiO_2 contents, as well as those for Fe_2O_3 and K_2O , which could lead to differentiated rheological behavior of the paste during geopolymerization chemical reactions. Moreover, the CaO content of batch 1 was almost 6 times greater than batch 2. This could be related to the higher viscosity of the paste produced using the first batch [10, 11]. This issue still requires a more extensive assessment in further research.

Following the preparation of the 7.5 M alkaline solution, a new mixture with metakaolin batch 2 was prepared. This geopolymer paste presented a similar rheological behavior to that obtained using 5 M alkaline activation. Therefore, it was impossible to execute the printing, even at 10 bar system pressure, quite possibly on account of water content, as it was reduced from 29.4% to 21.8%. It was once more opted to reduce molar concentration using a 7.4 M alkaline solution, resulting in a geopolymer paste that still posed some difficulties while flowing and the printed sample collapsed after only a five-layer deposition. Therefore, it was adopted an intermediate alkaline solution molarity of 7.45 M. Moreover, the plasticizer (HPMC) percentage was raised from 2% to 3%, given the paste flowing difficulty inducing a fine-tuning on material flowability as well [14]. These new parameters and printing pressure at 10 bar still offered some paste difficulties, once it took 12 min to flow from the pneumatic reservoir to the extrusion head. Nonetheless, it was possible to print 17 layers, but the sample collapsed under its own weight afterward once more. As the distance between the printed layers and the extrusion nozzle became longer, an irregular deposition of subsequent layers was observed (Fig. 5).

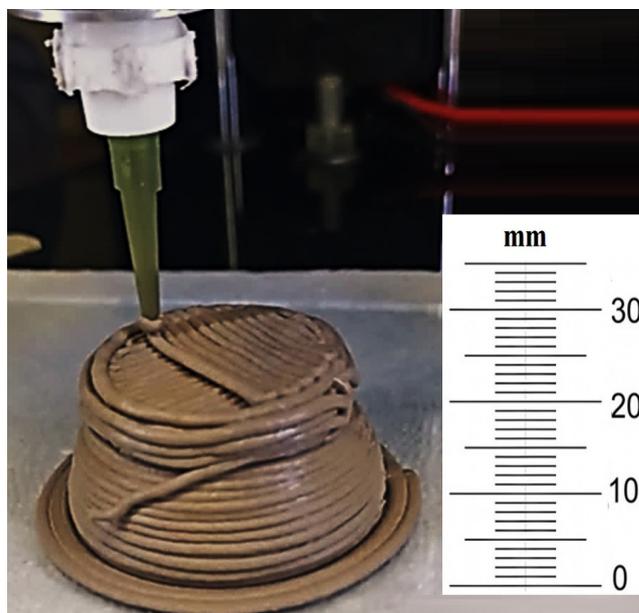


Figure 5: Image of a collapsed printed sample using geopolymer prepared using a 7.45 M alkaline solution.

A new geopolymer paste was prepared using an alkaline solution of 7.46 M. Besides, in order to improve the rheology with the available water of the mixture, a 2% surfactant was adopted. Furthermore, the hose coupled with the pneumatic reservoir was changed from a 90-degree format (Fig. 6a) to a straight format (Fig. 6b). Such a modification was enough to increase efficiency in paste flow through the hose. It was observed that the geopolymer paste at 7.46 M and under 10 bar pressure flowed from the pneumatic reservoir to the extrusion head in 4 min through the hose, and the printing

occurred with no major problems, thus producing a cylinder of desirable quality (Fig. 7).

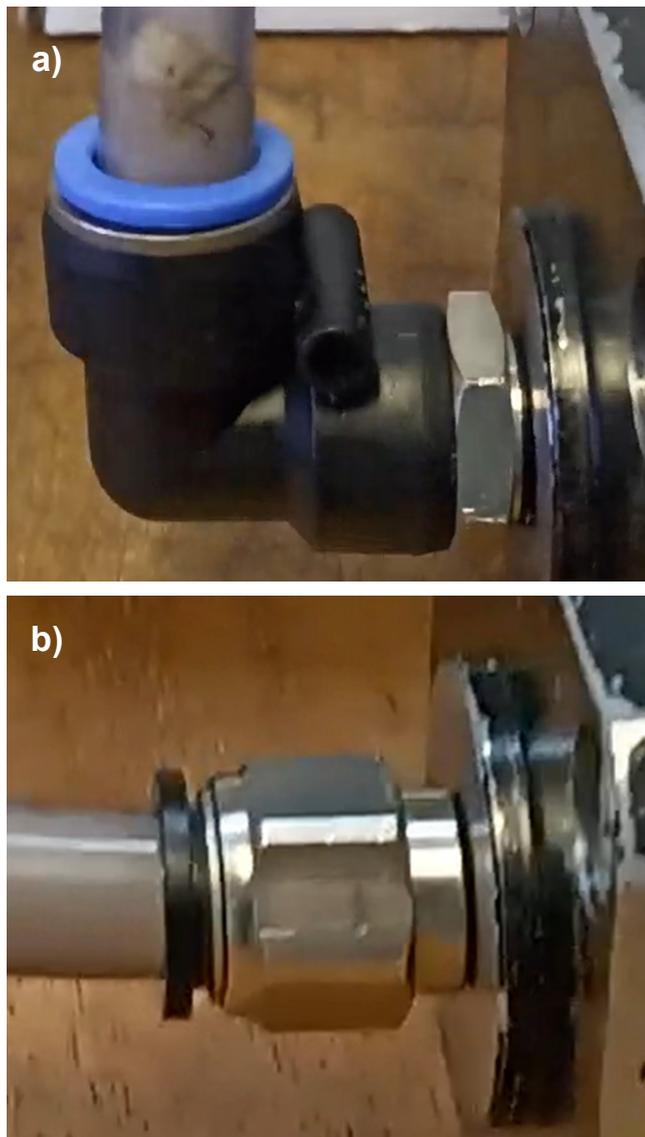


Figure 6: Images of hose coupling with 90-degree format (a) and straight-format (b).

With the last geopolymer formulation at 7.46 M, it was decided to add polypropylene fibers initially set at 0.25% of the total weight of the paste, resulting in a material capable of flowing from the reservoir to the extrusion nozzle within less than 1 min. However, there was clogging at the moment the paste reached the nozzle. Before a new printing test was carried out, the extruder bearing required change due to geopolymer blocking with fibers between the spheres, which revealed that the pressure was too high. Furthermore, fiber content was reduced to 0.05 wt% and a new geopolymer paste was prepared. Printing pressure was also naturally reduced from 10 to 7 bar, mostly to prevent the occurrence of a new failure on the retaining ring, in addition to protecting the bearing. The geopolymer paste with the PP fiber as reinforcement was inserted in the pneumatic reservoir and another printing test was initiated. The material

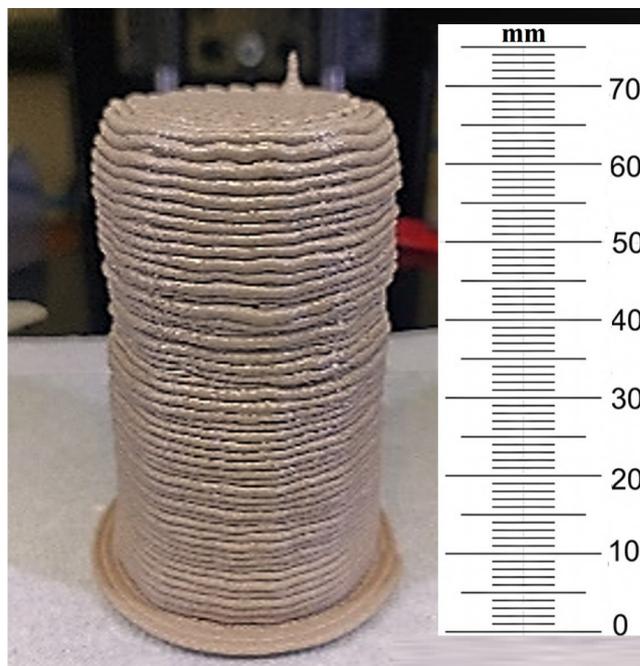


Figure 7: Image of cylindric geopolymer sample printed using metakaolin from batch 2 and 7.46 M alkaline solution.



Figure 8: Image of cylindric geopolymer sample printed using metakaolin from batch 2, 0.05% of PP fibers, and 7.46 M alkaline solution.

flow took 1.5 min to reach the extrusion nozzle and the specimen was printed (Fig. 8).

It is worth mentioning that all printing tests have been taken according to orientations regarding the parameter settings on the Ultimaker Cura software, and the printing patterns were kept

until the very end of the experiments [17-19].

CONCLUSIONS

The molarity of alkaline solutions affected water content directly and, consequently, the rheological behavior of geopolymer pastes. However, chemical composition and particle size distribution can also severely affect rheology, indicating that further research is required. Optimal formulations of metakaolin were successfully found for two batches. Both formulations with metakaolin from batches 1 and 2 and alkaline solution at 4.75 and 7.46 M, respectively, were suitable for 3D printing. The latter was performed with polypropylene (PP) fibers. It was noted that with 0.25 wt% content of PP fibers, an adequate extrusion nozzle to avoid any clogging is necessary. However, the printing of a cylindrical geopolymer paste sample with 0.05 wt% PP fibers content was possible. It was necessary to adjust the 3D printer pressure to enable the printing of cylindrical samples, both with and without fiber reinforcement. The printing parameters' settings on Ultimaker Cura software, such as head displacement speed, layer height, and thickness, were significant for achieving a uniform sample printing having a good appearance and dimensional stability. Higher head displacement speeds and lower material flow caused interruptions while depositing the layers.

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