



**HAL**  
open science

# Effect of Metakaolin, Fly Ash and Polypropylene Fibres on Fresh and Rheological Properties of 3D Printing Based Cement Materials

M. Dedenis, Mohammed Sonebi, Sofiane Amziane, A. Perrot, G. Amato

► **To cite this version:**

M. Dedenis, Mohammed Sonebi, Sofiane Amziane, A. Perrot, G. Amato. Effect of Metakaolin, Fly Ash and Polypropylene Fibres on Fresh and Rheological Properties of 3D Printing Based Cement Materials. RILEM International Conference on Concrete and Digital Fabrication, Jul 2020, Eindhoven University of Technology, Netherlands. pp.206-215, 10.1007/978-3-030-49916-7\_21 . hal-03086174

**HAL Id: hal-03086174**

**<https://uca.hal.science/hal-03086174v1>**

Submitted on 17 Jan 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# Effect of Metakaolin, Fly ash and Polypropylene Fibres on fresh and Rheological Properties of 3D Printing Based Cement Materials

M. Dedenis<sup>1</sup>, M. Sonebi<sup>1</sup>, S. Amziane<sup>2</sup>, A. Perrot<sup>3</sup>, G. Amato<sup>1</sup>

<sup>1</sup> Queen's University of Belfast, School of Natural Build Environment, Belfast, UK

<sup>2</sup> Université Blaise Pascal, Polytech Clermont-Ferrand, 63174, Aubière, France

<sup>3</sup> Univ. Bretagne-Sud, UMR CNRS 6027, IRDL, F-56100 Lorient  
m.sonebi@qub.ac.uk

**Abstract.** The aim of this paper is to investigate the effect of mix composition such as the percentages of metakaolin (MTK) and fly ash (FA) on the fresh and rheological properties and also the percentage of polypropylene fibres. Several tests were used to determine the rheological properties such as the flow table test, the cylindrical slump test and penetrometer test. The estimated yield stress values were then calculated from the results of cylindrical slump test and the fresh density of mortar.

The extrusion of layers for 3D printing was carried out using a controlled air pressure gun. This tool made it possible to test the extrusion of each mortar mix directly after mixing by producing several layers on top of each other. The use of MTK had a significant effect on the fresh and rheological properties. It was observed that replacing cement with MTK led more cohesive and dry mixes and therefore difficult to extrude. Using a combination of FA and MTK has increased the yield stress, cohesion, reduced the penetration and improved the shape stability and printability. It also reduced bleeding and segregation. Finally, adding more polypropylene fibres reduced the workability by improving the cohesion with a denser fibre network and reduced the penetration. Thus led to an increase in the yield stress and a reduction of the fresh properties. Good relations were observed between the fresh and rheological properties.

**Keywords:** 3D Printing; Metakaolin, Polypropylene Fibres, Penetration; Slump flow; yield Stress

## 1 Introduction

3D printing in civil engineering includes four different processes that have been invented so far: Contour Crafting (US), Concrete Printing (UK), D-shape (Italy) and Smart Dynamic Casting (Switzerland). Among digital concrete methods, extrusion-based 3D printing is probably the most developed technique. Recent researches on 3D printing have conducted some investigations on the mix-design, rheological and process related issues [1-6].

Concerning binder's composition, it has been concluded that adding 24% of fly ash, 8% of silica fume and using natural fibres from 0.2 to 0.6% results in great printability properties, improvement in rheological and fresh performances and in bleeding and segregation resistance. Plus, the addition of nanoclay-based viscosity modifying agent (VMA), Actigel, has proved to be efficient in developing 3D printing essential characteristics [5, 6].

The objective of this study is to evaluate the effect of different mix compositions such as 10 to 15% of metakaolin, 30% of fly ash and percentage of polypropylene fibres (1.2 to 3.6 kg/m<sup>3</sup>) on the fresh and rheological properties of a printable mortar using layers extruded with a simple modified joint gun, and the rheological and fresh properties of different mix designs were evaluated.

## 2 Printing process

The essential properties for a mortar to be printable are: extrudability and the resistance to deformation of the layers under their own weight and that of the following layers at fresh state. Both parameters depend on the rheological properties of the fresh cement paste [7, 8].

Extrudability is associated with the ability of the material to pass through the nozzle of the printing equipment, depending on its consistency and workability of the mixture. For a mortar to have good workability, bleeding and segregation must be avoided, and the mortar must be not too fluid in order for each printed layer to sustain its own weight and the weight of the upper layers. Extrudability is mainly influenced by the water/binder ratio, sand/binder ratio and chemical additives of the mix design such as superplasticiser [4-6].

In addition to low deformability at fresh state, layers must also bind to each other to form a uniform and rigid whole. This layer bond depends mainly on the printing process (time between deposit), nature of surface layer and mix proportions. The printability of a mortar can be assessed through the opening time. This parameter, also called time interval, represents the maximum time interval over which printability can be achieved in a suitable way. Opening time should be neither too long nor too short. If the time interval is too long the bonding between the layers will be weak, while if it's too short the mortar will be unextrudable [1].

## 3 Experimental programme and methods

In this investigation, the 3D printing was carried out by extruding layers of mortar with a compressed air gun. The compressed air gun had a capacity of  $5.2 \times 10^{-4}$  m<sup>3</sup>. A single pressure of 2 bar was used for all mixes. The shape of the nozzle was carefully chosen to achieve cross section of 24x14 mm<sup>2</sup>. The nozzle had a ribbed inner surface to ensure good cohesion between the superimposed layers. The effects of addition of PP from 1.2 to 3.6 kg/m<sup>3</sup> in reference mix, replacement of cement by 30% FA, and replacement of cement by 10 to 15% MTK were investigated on fresh properties and extrudability of 3D printing mortars.

### 3.1 Mix design

Table 1 presents the mixtures investigated in this research. The binder used was an ordinary portland cement CEM1 52.5 N according to BS EN 197-1:2011. Fly ash (FA) with particle density of 2210 kg/m<sup>3</sup> complied with BS EN 450-1:2005+A1:2007. Metakaolin (MTK) is a highly processed form of kaolin clay, which is a mineralogically complex hydrous aluminium silicate, white in colour with a dull lustre. It is a processed material, calcined in kilns to form highly reactive material known as MTK. MTK is a pozzolan, which is a material that, when mixed with water will chemically react with calcium hydroxide at normal temperatures to form compounds possessing cementitious properties (density = 2.2 kg/m<sup>3</sup>).

The sand used had particle size between 0 and 4 mm, absorption coefficient of 0.30 and density of 2650 kg/m<sup>3</sup>. Before mixing the sand was dried and sieved with a 1.18 mm sieve using a shaking table. The sieve size was chosen to obtain a thinner paste and therefore achieve a better extrudability of the mortar and an easier printing process. Moreover, this particle size allowed using a viscometer.

The sand/binder and water/binder ratios were kept constant for all mixes at 2 and 0.5 respectively. Similarly, the water temperature was maintained at around 16°C for all mixtures.

SP from modified polycarboxylic ether fluid was used as an aqueous solution with a solid content of 30% and specific gravity of 1.05. Polypropylene (PP) fibres were also used which are monofilament FIRBIN fibres with 6 mm long and diameter of 100 µm. The fibres used at dosage of 1.2 and 2.4 kg/m<sup>3</sup>.

The mixing procedure required the use of a 2.5 L capacity mixer. To avoid materials to go over the mixing bowl while the mixer is on, different volumes of cement paste have been calculated up to 2.2 L. This blender allows two different speeds, which will be referred to later on by low (140 rpm) or high speed (285 rpm). First of all, dry materials are positioned in the mixer: binders as cement and fly ash, and sand. In order to obtain a good particles repartition, the blender is turned on for 30 seconds, on the first speed (low).

Secondly, water mixed with superplasticiser is inserted into the mixing bowl: this is when the time counting starts ( $t = 0$ ). Binders, sand, water and SP are then mixed for 30 seconds at low speed. Finally, PP fibres are added to the mix and blended for 30 seconds at low speed.

To ensure good repartition of fibres and a proper cohesion of materials, the mix is blended for 2 minutes at high speed. Finally, the mixture is blended a last time at low speed for 1 minute for the mixture to settle. At this stage, the mortar is tested for rheological and fresh characterisation, as described in the test methods section.

**Table 1.** Mix design of mortar tested (kg/m<sup>3</sup>).

Mix Code	C	FA	MT K	W	Sand	SP	PP
REF-PP1.2	607	0	0	305	1230	0.136	1.2
REF-PP2.4	607	0	0	305	1230	0.136	2.4
REF-PP3.6	607	0	0	305	1230	0.136	3.6
FA30-SP0.2-PP1.2	435	172	0	305	1205	1.213	1.2
FA30-SP0.2-PP2.4	435	172	0	305	1205	1.213	2.4
REF-MTK15-SP0.44-PP1.2	516	0	91	305	1225	2.671	1.2
FA30-MTK15-SP0.44-PP1.2	334	182	91	305	1180	2.671	1.2
FA30-MTK10-SP0.44-PP1.2	364	182	61	305	1184	2.671	1.2

### 3.2 Testing procedure

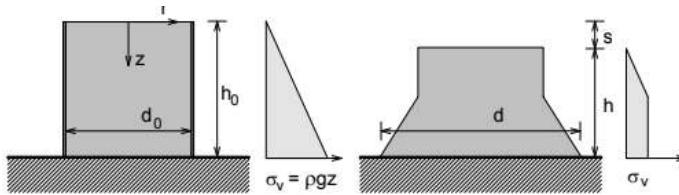
Two simple tests have been performed on every single mortar mixture to define the fresh properties of mortar: the penetrometer test and the flow table test. In order to describe pastes rheological properties, a semi-empirical test, slump test, have been employed. Indeed, right after mixing, the first test is the penetrometer test, followed by the flow table test and then by the slump test. The duration of every test (penetrometer, flow table, cylindrical slump test, density) was carried out in less than 3 min  $\pm$  1 min. After that, the density of the mix is measured. It is important to note that the mortar is mixed by hand during 15 seconds before each test and the density measurement.

The standard BS ISO 13765-1:2004 characterises the use of the cone penetrometer. In fact, this test aims to determine the workability and the consistency of the mortar under a certain stress caused by the dropping cone (only under gravity). Firstly, the cement paste is introduced in the conical mould in two layers. In order to have a homogeneous filling and to avoid voids in the moulds, each layer is compacted with ten short strokes. The excess of mortar is removed using a trowel or a spatula and the mould is placed under the dropping cone. Then, the testing machine is adjusted so the cone just touches the surface of the sample. Finally, the button is pressed for 5 seconds and the cone is released: it penetrates into the mortar sample under its own weight. The value read on the dial is noted: this penetrometer allows a precision of 0.01 mm. The cone is then dropped 3 more times in order to have more values and so the mean value will be more precise.

The flow table test was used to measure the stiff mix consistency by taking the spread of the mortar under a certain type of stress (jolting; BS EN 1015-3:1999). The first step is to place the conical mould centrally on the flow table. The mortar is then introduced in two layers; each layer is compacted by ten strokes. The mould must be maintained properly when filling it. The excess of mortar is then removed. After 15 seconds, the mould is slowly and vertically lifted: two values of both diameter of the slump (two perpendicular directions) and height are measured. Finally, the sample is

spread out on the flow table by jolting: 15 jolting in 15 seconds are required. Afterwards, measurements are taken another time: two perpendicular diameters of the spread.

The third test is quite similar in execution then the previous one: the slump test. Indeed, the procedure followed for this test is similar to the flow table test, previously exposed: the cylindrical mould is centrally placed onto the flow table; the mortar is introduced in two 10-strokes-compacted layers into the mould (firmly maintained); the excess of mortar is removed to have a plain surface and the mould is lifted after 15 seconds; finally, two values of both heights and diameters are written down in order to have more precise averages. However, this semi-empirical test allows estimating the static yield stress of the mix depending on the ratio height/spread. Three different flow regimes exist with an important stress tensor difference: when  $H \gg R$ ,  $H \approx R$  and  $H \ll R$  – where  $H$  is the height and  $R$  is the radius after the mould's lift [7] – See Fig. 1.



**Fig.1.** Notations for estimating the yield stress with the slump test [7]

After these previous tests, the density is taken in a cylindrical mould filled with two layers of mortar, each of them compacted by 10 strokes.

For the opening time procedure, every time 15 min of measurement, the mortar was remixed and the tests were conducted such as the penetration test, the flow table and the slump test through time during 135 minutes.

## 4 Results and discussion

### 4.1 Fresh and rheological properties

In this section the results of the penetration test, flow table, slump test and portable vane carried out on the different mixtures are reported and discussed. All results are summarized in Table 2.

**Table 2.** Fresh and rheological results [ $\text{kg/m}^3$ ]

Mix	Penetrometer (mm)	Flow Table Spread (mm)	Slump Test (mm)	Vane test Yield Stress (Pa)
REF-PP1.2	33.3	224.0	110.0	1286
REF-PP2.4	21.3	213.5	113.5	1360
REF-PP3.6	20.0	173.5	124.0	1507
FA30-SP0.2-PP1.2	38.6	233.0	106.5	1334
FA30-SP0.2-PP2.4	29.6	205.5	117.0	1674
REF-MTK15-SP0.44-PP1.2	28.2	190.0	121.5	1464
FA30-MTK10-SP0.44-PP1.2	28.7	200.0	122.0	1444
FA30-MTK15-SP0.44-PP1.2	36.4	206.0	117.0	1369

#### 4.2 Effect of binders and fibres

It was observed that fly ash improved the extrusion of mortar, and can be extruded for long time compared to reference mix (100%C) due to none-early reaction of FA (see section 4.4). Mix with FA helped also to have a better cohesion between layers. However, as shown in Table 2, adding Fly Ash has opposite effect on the two reference mixes which differ only by the amount of PP fibres. The fact that bleeding is reduced when FA is added may be explained by the size and shape of the particles. The surface area of FA particles is  $420 \text{ m}^2/\text{kg}$  while that of cement is  $370 \text{ m}^2/\text{kg}$ , therefore more water is needed to cover the surface of the particles. In addition, cohesion and segregation improved and reduced respectively by replacing part of the cement with FA, due to the ball bearing effect of the particles. FA is known as an extrusion improving additive because the spherical shape of its particles acts to decrease rheological parameters (yield stress and plastic viscosity). However, the increased FA content may result in reduced workability due to absorption of the SP [8].

As FA, also MTK allows for better extrusion, longer extrusion time and better buildability and cohesion of the layers. MTK particles have a flat shape with a very large specific surface area per unit volume. In addition, the silicate and aluminate contained in the MTK make pozzolanic particle surfaces reactive. These properties of MTK particles have led to an extremely high water demand. As a result, the pore volume of the binder has been greatly reduced due to the efficient consumption of water in hydration reactions [9].

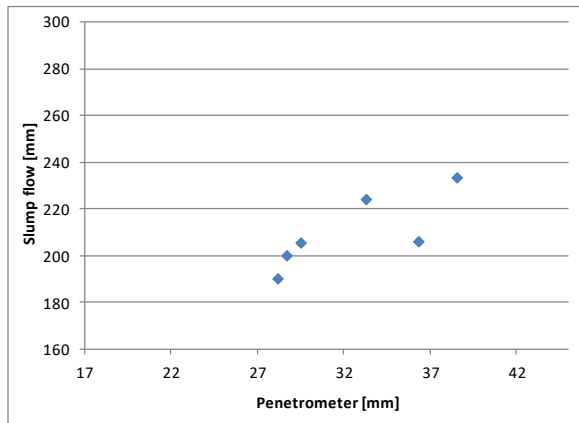
As the specific surface of MTK is equal to  $1410 \text{ m}^2/\text{kg}$  while that of cement is  $370 \text{ m}^2/\text{kg}$ , bleeding reduced considerably and cohesion improved, which explains the greater fresh and rheological properties obtained with a higher MTK dosage. We can therefore conclude that metakaolin is a suitable material for 3D printing since it improves the rheological properties of mixes. Moreover, adding 15% metakaolin is more beneficial than a 10% dosage.

When FA is added to MTK, the rheological properties are homogeneous. As the slump flow decreases this confirms the usefulness of MTK in cementitious mixtures

for 3D printing. The increase in fibre content affected the handling and cohesion of the material. The fibres created a connected mesh that improved the fresh and rheological properties as better cohesivity of the mix which led a better buildability and stability of the shape of layers. However, high percentage of fibres can lead a blockage of mortar in the gun [4-6].

### 4.3 Correlation of rheological properties

The flow table and penetrometer tests are good indicators for determining the consistency of mixtures and therefore the workability of the mortar. These measurements correspond to the fluidity of the material or, conversely, its cohesion, and make it possible to evaluate its deformability of the material when it is subjected to a certain type of stress. In Fig. 2, the slump flow values are plotted as a function of penetration. As expected, this figure shows that when slump flow increased, the penetration also increased.



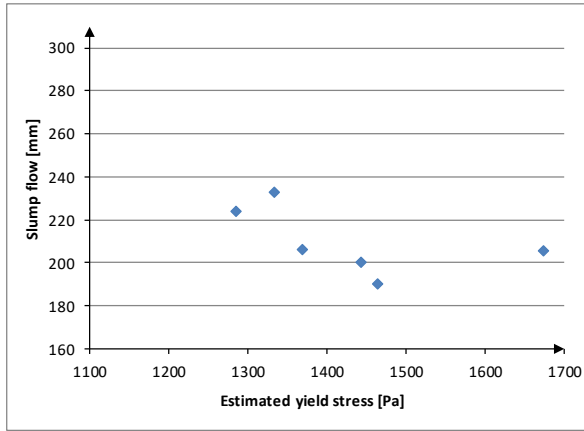
**Fig. 2:** Variation between slump flow and penetration

The main parameter that can be determined from this experimental program is the yield stress of the mixtures. Due to the need for a rigid mixture to be extrudable, the yield stress of the mixtures studied cannot be evaluated using the traditional rheometer. Therefore, a semi-empirical formula is used which links the static yield stress to the deviations and heights of the cylindrical collapse test.

As mentioned previously, three regimes are used to estimate this rheological parameter:  $H \ll R$ ,  $H \approx R$  and  $H \gg R$ . In this case,  $H \ll R$ , i.e. fluid mortars, was not appropriate. Depending on whether the cement paste has an intermediate or rigid consistency, the cases  $H \approx R$  and  $H \gg R$  are used according to the visual ratio and the  $R/H$  ratio [7].

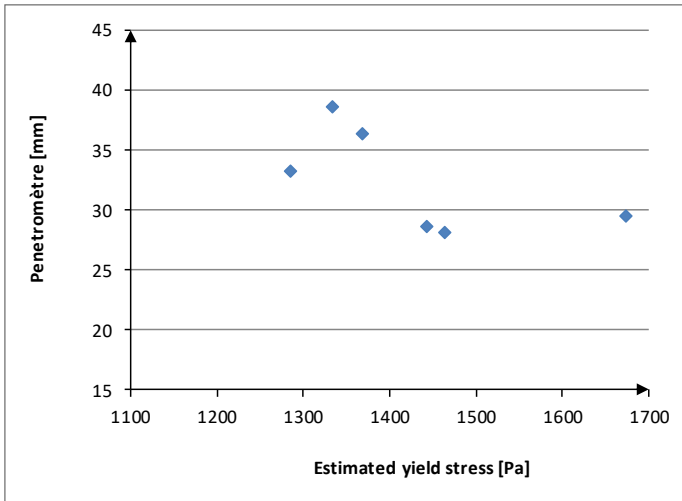
The previous analysis of fresh and rheological properties shows a certain link between the flow table and the estimated yield stress. Generally, when the slump flow reduced, the estimated yield stress increased. This trend can be observed in Fig. 3 which presents all the results of this investigation.





**Fig. 3:** Variation between slump flow and yield stress

Fig. 4 presents all penetration results as a function of the estimated yield stress values. The graph shows that penetration and yield stress estimation are inversely proportional: the greater the estimated yield stress increased, the lower was the penetration value.



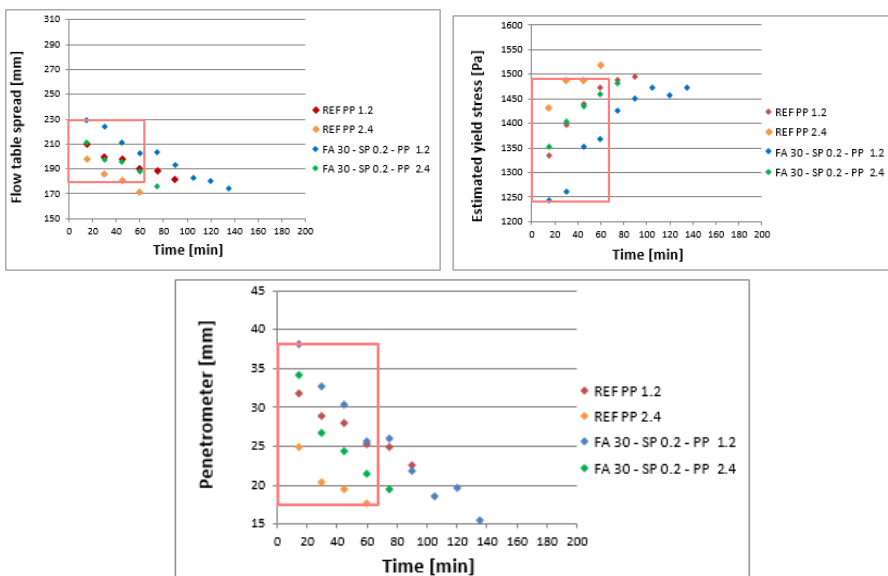
**Fig. 4:** Variation between penetrometer and yield stress

#### 4.4 Opening time

Fig. 5 shows the flow test results and estimated yield stress measured at different testing times up to 140 min. As it can be observed the curves of the two reference mixes have better estimate of yield stress and lower penetration and flow compared to the fly ash mixtures. This suggests that fly ash takes longer to react. Indeed, the pozzolanic behaviour of FA and the size of its fine particles improve the fresh and rheological properties of mixtures but only after a certain time. As a result, FA can help to

maintain the consistency and workability of the mortars over a longer period of time. The limit of observed mixture printability has been also plotted describing printable boxes for each formulation.

As also shown in Fig. 5, the estimated yield stress increased with a higher amount of PP fibres in the mixture, while penetration and flow decreased. This can be due to a larger mesh size created by the fibres which make it is more difficult for the cone of penetrometer to penetrate in the mortar. Similarly, this mesh size allows the flow to be retained during the flow table test. Rheological properties are therefore improved with an optimum of fibres. However, high addition of fibres can create an increase in connectivity of network between fibres and can prone to stiff mix leading to possible of reducing the extrusion time.



**Fig. 5:** Printable box of 3D printing mortar

## 5 Conclusions

This experimental study aimed to analyse the effects of different mix components on the rheological and fresh properties of 3D printable mortars. The different mixes were assessed based on the results of penetration test, flow table, the portable vane. Rheology was evaluated by determining the estimated yield stress. Mortar layers were produced by extrusion using a compressed air gun.

Based on the above tests the following conclusions can be drawn:

- FA and MTK increased the fresh and rheological properties of the mortars and the optimal mix proved to be a combination of both components in terms of workability and extrudability.

- The use of MTK in combination with cement appears to have a significant impact on the behaviour of 3D mortar. The mix showed to be more rigid and dry and therefore difficult to extrude.
- Using a combination of FA and MTK increased the yield stress, cohesion, stability and printability. It also reduced the bleeding and segregation and improve the stability.
- The fibres reduced the slump flow by improving cohesion through a denser fibre network. The highest percentage of fibres led to an increase of the yield stress and decrease of workability.
- Printability box with opening time was established for the mixes investigated in this paper.

## References

1. Perrot, A. 3D Printing of Concrete: State of the Art and Challenges of the Digital Construction Revolution (2019); Wiley-ISTE; ISBN 1-78630-341-8.
2. I.V. Mechtcherinea, F.P. Bos, A. Perrot, W.R. Leal da Silva, V.N. Nerella, S. Fataei, R.J.M. Wolfs, M. Sonebi, N. Roussel, "Extrusion-based additive manufacturing with cement-based materials – Production steps, processes, and their underlying physics: A review", CCR Vol 132, 2020, 106037, <https://doi.org/10.1016/j.cemconres.2020.106037>.
3. Perrot, A.; Rangeard, D.; Pierre, A. Structural built-up of cement-based materials used for 3D-printing extrusion techniques. *Mater. Struct.* 2016, 49, 1213–1220.
4. Bohuchval, M., Sonebi, M., Amziane, S., Perrot, A. (2020) "Rheological properties of 3D printing concrete containing sisal fibres", Proceedings of the third International Conference on "Bio-Based Building Materials", Academic Journal of Civil Eng. Special Issue, 37(2):249-255.
5. Rubio M., Sonebi M., Amziane S. (2017) Fresh and rheological properties of 3D printing bio-cement-based materials, Proceedings of 2nd ICBBM (PRO 119), pp. 491-499.
6. Rubio M., Sonebi M., Amziane S. (2017) 3D printing of fibre cement-based materials: fresh and rheological performances, Proceedings of 2nd ICBBM (PRO 119), pp. 284-291.
7. Coussot P. and Roussel N., Fifty-cent rheometer for yield stress measurements: From slump to spreading flow (2005), The Society of Rheology, Inc. *J. Rheol.* 49(3):705-718.
8. Sonebi, M., Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash, *Cement & Concrete Res.*, 36(9), 2006, 1609-1618.
9. Sonebi, M., Lachemi, M., Hossain, KMA. (2013) Optimisation of Rheological Parameters and Mechanical Properties of Superplasticised Cement Grouts Containing Metakaolin and Viscosity Modifying Admixture, *Construction and Building Materials Journal*, 38(1):126-138.