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Influence of Supplementary Cementitious Materials on Fresh Properties of 3D Printable Materials

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Abstract: The development of printers and materials for 3D Printing Construction during the last two decades has allowed the construction of increasingly complex projects. Some of them have broken construction speed records due to the simplification of the construction process, particularly in non-standard geometries. However, for performance and security reasons the materials used had considerable amounts of Portland cement (PC), a constituent that increases the cost and environmental impact of 3D Printable Materials (3DPM). Supplementary Cement Materials (SCM), such as fly ash, silica fume and metakaolin, have been considered a good solution to partially replace PC. This work aims to study the inclusion of limestone filler, fly ash and metakaolin as SCM in 3DPM. Firstly, a brief literature review was made to understand how these SCM can improve the materials' 3DP capacity, and which methods are used to evaluate them. Based on the literature review, a laboratory methodology is proposed to assess 3DP properties, where tests such as slump and flow table are suggested. The influence of each SCM is evaluated by performing all tests on mortars with different dosages of each SCM. Finally, a mechanical extruder is used to extrude the developed mortars, which allowed us to compare the results of slump and flow table tests with the quality of extruded samples.

Keywords: 3D printing; construction; materials development; fresh properties; supplementary cementitious materials

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Citation: Teixeira, J.; Schaefer, C.O.; Maia, L.; Rangel, B.; Neto, R.; Alves, J.L. Influence of Supplementary Cementitious Materials on Fresh Properties of 3D Printable Materials. *Sustainability* **2022**, *14*, 3970. https://doi.org/10.3390/su14073970

Academic Editors: Marc A. Rosen, João Almeida, Nuno Simões and Julieta António

Received: 14 February 2022
Accepted: 24 March 2022
Published: 28 March 2022

1. Introduction

Three-dimensional Printing Concrete (3DPC) is an innovative method that brings the benefits of optimizing the process, in time, cost, materials and energy management and design flexibility. These advantages provide greater customization capacity in construction, without a high environmental and economic impact. Two techniques of 3DPC are currently used, namely particle bed deposition [1] and extrusion-based technique [2]. During recent years, different types of constructions have been printed using the extrusion-based technique, breaking records of construction time and efficiency in resource management. SQ4D Inc. company (New York, United States of America), the creator of the first 3D-printed house for sale in the United Sates, proposes to print houses three times faster and 40% cheaper than conventional methods, with zero waste and low energy consumption [3]. This is an offer that results from the strong investment in the development of a highly technological printer and materials. The commitment to the material and technology development for 3DPC is being driven by challenges launched by large entities and governments.

NASA promoted a "3D-Printed Habitat Challenge" for the development of a printed habitat beyond our planet [4]. The city of Dubai committed to printing 25% of all new buildings until 2025, a construction strategy announced in 2016 with the aim of reducing labour by 70% and cutting costs by 90% [5].

Presently, there are 3D printers that provide the construction of several types of on-site structures or in a prefabrication environment, however, the purchase of high-performance equipment is still very high [6], making its dissemination difficult. This problem has led many research centres to focus on material exploration in laboratory small sets, allowing the evaluation of the printing mortar's properties on small and medium scale structures. This problem proves that 3D printing (3DP) is not yet a constructive process of unequivocal value for on-site constructions, however, it can be very useful when used in prefabrication production. The creative freedom that this offers to prefabrication, reducing the industrial process and its consequential high environmental costs and impacts, could be a good way to optimize customization in construction.

The company Twente Additive Manufacturing (TAM) is a good example of customization using 3DPC. This company has explored the textures given by 3DP layers as an aesthetic element in facade panels and walls [7]. In 2016, Bruil exhibited the results of the colour grading studies in the Material Xperience exhibition in Rotterdam [8]. These examples show that 3DP offers great possibilities for architects, designers and engineers to explore complex geometries, textures and colours. To achieve this creative freedom, it is necessary to develop materials capable of providing a good surface finish on the printed structure. PC has been proved to be a suitable 3DP ingredient owing to its inherent thixotropy property. However, for performance and security reasons, the materials used by the printers have considerable amounts of PC in their composition, a constituent with a great environmental impact due to its high energy consumption and CO_2 emissions during clinker production [9]. While in ordinary concrete, PC quantity is 270–350 kg/m^3, the literature shows compositions for 3DP using between 298 kg/m^3 [10] and 900 kg/m^3 [11,12].

Recently, researchers have tried to find more sustainable materials to reduce the negative environmental effect generated by PC. In 3DPM, coarse aggregates should not be used, with the amount of paste being crucial for the material to be pumped and extruded. The paste works as a binder and lubricant during the printing process, so a 3DPM requires a large amount of powder in the material's composition. In this way, the inclusion of Supplementary Cement Materials (SCM) to partially replace the PC can be a way to reduce the environmental and economic impact of 3DPM, without harming its properties. The most used are fly ash (FA), silica fume (SF) [10,13–21], metakaolin (MTK) [22–25], limestone filler (LF) [25] and nanoclays (NC) [11,12,26]. They can improve the material's workability, mechanical performance, durability, dimensional stability and reduction of hydration heat.

In the fresh state, a 3DPM must show an evolution in workability, initially requiring a very workable material to be easily transported from the mixture to the extruder. After extrusion, it should lose part of this workability, stiffening, to be extruded into uniform filaments capable of supporting subsequent layers without deformations. This transformation is necessary over the 3DP process and can be defined in the following 3DP properties: pumpability, extrudability, shape retention and buildability, the period in which the material fulfils all these properties is called open time [16,27].

The workability is related to mortar consistency, indicating a greater or lesser aptitude to be handled. Particle size, specific surface and paste/aggregate volume are directly related to workability [16,22,28,29]. Mixtures with a high powder content result in a better packing of the particles that act as lubricants, making the mixture more workable [30]. It is a characteristic that makes pumping and extrusion easier but increases the possibility of layer deformation or collapse [11,14,23,31]. The workability can be controlled with the following tests: flow table [12,16,32,33], slump flow [23] and V-funnel [16,34]. Extrudability, directly related to workability, is the mortars' ability to be extruded through a nozzle into continuous, uniform and stable filaments without blocking the system [11,14,23,31]. Usually, it is measured visually by controlling the quality of the extruded filaments [11,14].

Shape retention and buildability are important due to the absence of formwork, the material needs to maintain its shape by gaining stiffness to support stacked layers without deformations. This stiffness gained should not compromise the bonding between layers, with some moisture in the material being necessary to promote good adhesion. The formwork absence makes the material depend on the internal cohesion between paste and aggregates, with a high static yield stress being required [11,29,31]. Usually, buildability is evaluated by extruding filaments into stacked layers [32]. Open time represents the time when the material can be extruded without blocking and stacked in layers without deformations. Printability describes the ability of a material to be printed in various geometries maintaining dimensional stability and good surface finish, depending not only on the properties in the fresh state but also in the hardened state. [35].

The dosage and preparation of 3DPM must consider the compatibility between the material and the printer. Factors such as the mixing procedure, pump capacity, shape and size of the nozzle and type of extruder must be considered [16,33]. Usually, there is an increase in cement consumption and a reduction in sand content to improve 3DP properties. For Kazemian et al. [11], a 3DPM is characterized by the absence of coarse aggregates, a high paste content and use of chemical additives.

A large amount of powder is required for a 3DPM, so using Supplementary Cementitious Materials (SCM) is essential to reduce PC content. They interact chemically and physically with the PC hydration. They modify the paste microstructure bringing advantages in technical, economic and sustainable aspects. Industrial by-products (FA and SF) or materials whose production cost is lower than Portland cement (MTK and LF) are examples of SCM, options that reduce cost, energy and CO_2 emissions. Technically, one of the main reasons for using them is to increase mechanical performance and durability, particularly pozzolans (FA, MTK and SF) due to the pozzolanic reaction. In 3DP, these materials are being used to optimize the fresh properties, however, the influence of each SCM is still not clear.

FA and SF are the most used combination of SCM in 3DP [10,13–19,36]. FA is normally used in greater amounts, about 20 wt% of the paste [15–18,22]. The spherical shape of its particles improves the material's workability, which is good for pumpability and extrudability, however, it may worsen its buildability [22]. This might be countered using other SCM in the composition, namely MTK [22–25], SF [11,12] or NC [11,12], whose inclusion improves buildability. Dedenis et al. [4] showed that using a combination of PC, FA and MTK increased the yield stress, cohesion, stability and printability, and was more effective than using just one of them in combination with PC. Zhang et al. [12] have proven that replacing 4 wt% PC with 2 wt% SF and 2 wt% NC provides greater buildability than compositions with just SF or NC. The study of Kazemian et al. [11] showed that the inclusion of 0.3 wt% NC allows a buildability similar to a mortar with 10 wt% SF. Bohuchval et al. [25] studied the inclusion of FA, LF and MTK in 3DPM, and noticed that replacing 24 wt% of PC by LF increased the material's workability making the mortar unsuitable for 3DP. On the other hand, replacing PC by 22 wt% of FA and 12 wt% of MTK showed appropriate properties for 3DP.

To summarize, the studies revealed that when PC was replaced by only one SCM, it was difficult to obtain adequate 3DP properties [25]. The best results have been achieved by combining different SCM. When using FA and LF (which tend to increase workability), it could be necessary to use other SCM capable of improving buildability/shape retention, this combination is essential for the mixture to reach the necessary balance for 3DP.

The aim of this study is, therefore, to synthesize the SCM commonly used in 3DPM, specifying the influence of each one on fresh properties. In addition, it mentions the tests that can be used to evaluate each 3DP property in the fresh state. Finally, a laboratory methodology is proposed to demonstrate the influence of LF, FA and MTK as SCM on fresh properties of 3DPM.

Contrary to the literature, the present study proposes an approach without any plasticizer or superplasticizer so that the influence of each SCM is clarified without its influence.

2. Materials and Methods

2.1. Materials and Mix Design

Ordinary Portland cement (CEM I 42.5 R), according to European Standard EN 197-1 (2011), also LF, MTK and FA as SCM, were used in the binder composition. Two different river sands, S1 and S2 (maximum particle size of 2 mm and 4 mm, respectively), were used as aggregates. All the mixtures developed presented 50% of paste volume and 50% of sand volume, where PC consumption varied between 232 kg/m^3 and 641 kg/m^3. Trying to understand the influence of each SCM in 3DP fresh properties, the mix design followed these steps: (i) compositions studied without any type of SCM; (ii) LF was chosen as the main SCM, and its influence was studied individually; (iii) the remaining SCM were studied by combining LF + FA (not recommended by the previous bibliographic study) and LF + MTK (recommended by the previous bibliographic study). The water/powder (w/p) ratio was obtained by performing several compositions in slump and flow table tests, starting with a composition with a high water content and decreasing it. Only compositions with a flow table test lower than 200 mm were tested in the mechanical extruder. Table 1 shows the mix design of all developed mortars.

Table 1. Mix design of studied mortars (kg/m^3).

Mortar	PC	LF	FA	MTK	W	S1	S2	*w/p*	R (% by Cement Volume)
PC-1	623	-	-	-	253	132	1187	0.41	-
PC-2	641	-	-	-	247	132	1187	0.39	-
LF-1	312	271	-	-	253	132	1187	0.43	50% LF
LF-2	330	287	-	-	241	132	1187	0.39	50% LF
FA-1	231	230	122	-	241	132	1187	0.41	40% LF + 25% FA
FA-2	241	240	127	-	232	132	1187	0.38	40% LF + 25% FA
MTK-1	233	101	-	82	304	132	1187	0.73	25% LF + 25% MTK
MTK-2	256	111	-	91	289	132	1187	0.63	25% LF + 25% MTK

PC—Portland cement; LF—Limestone filler; FA—Fly ash; MTK—Metakaolin; W—Water; S1 and S2—River sands; w/p—water/powders ratio; R—Replacement.

2.2. Methods

The above compositions were mixed following the procedure shown in Figure 1.

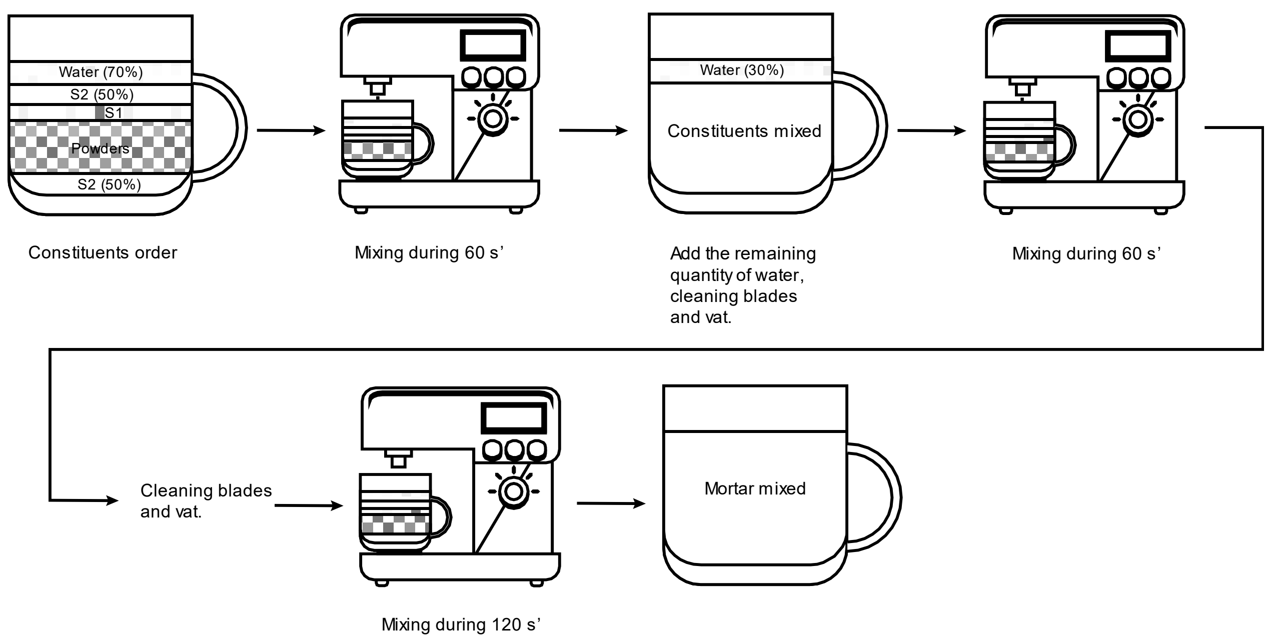

Figure 1. Mixing procedure of compositions in Table 1.

After mixing, the methodology represented in Figure 2 was performed. The methodology is divided in two phases: in the first, workability was controlled using the flow table and slump tests; and in second one, extrudability, buildability and shape retention were qualitatively evaluated using a mechanical extruder with manual movements and a circular nozzle (20 mm opening). During extrusion, the nozzle height was set at 15 mm in the first layer and 10 mm in the remaining layers, another important parameter such as the printing speed could not be evaluated since the printing table movements are manual. However, the system allows for layering, which is the basic principle of 3D printing. Figure 2 describes the whole procedure.

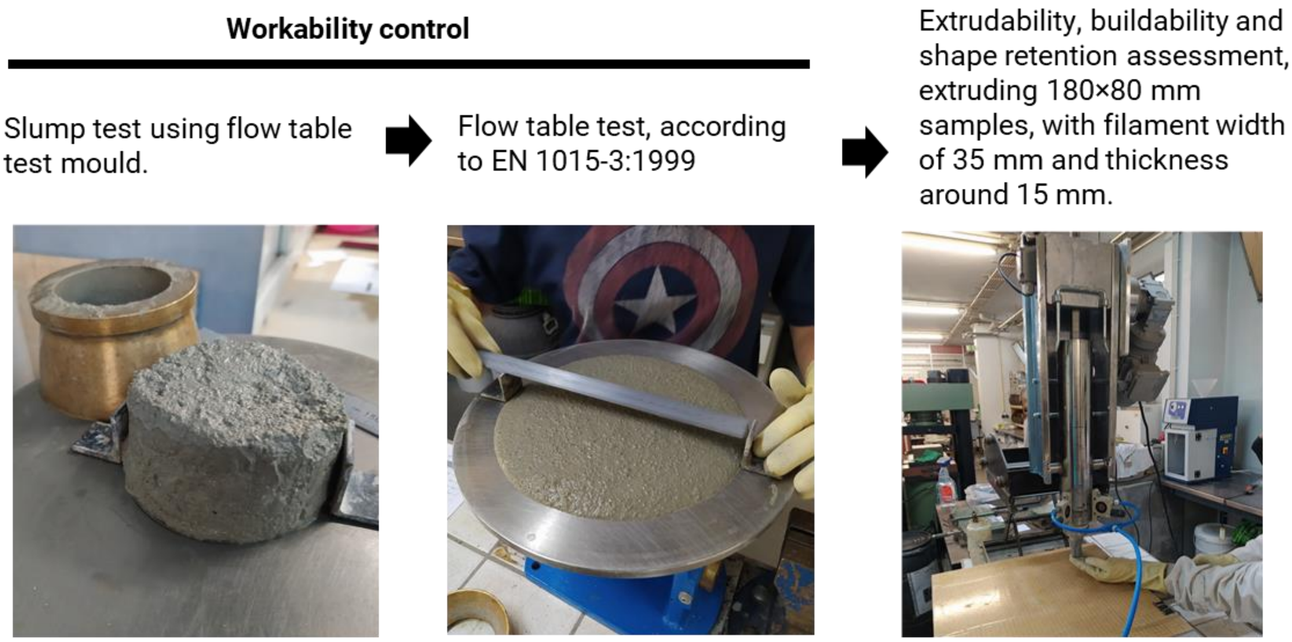

Figure 2. Laboratory methodology to evaluate workability, extrudability, shape retention and buildability; the entire procedure was carried out on the same batch, and each mortar was tested once.

3. Results

The results of the flow table and slump tests are graphically reported in Figure 3a. In addition, the capacity for 3DP was evaluated by extruding the material in samples with at least four layers [27]. All the mixes were extruded except the mix PC-2 because it was very dry and blocked the nozzle. Figure 3b illustrates the samples built by extrusion. The mixes PC1 and MTK-2 presented low workability and provided extruded samples with a large number of voids. Contrarily, the mixes LF-1 and MTK-1 presented high workability and provided extruded samples with deformed layers close to collapse. The mixes LF-2, FA-1 and FA-2 showed to be appropriate for creating 3D printing elements. Combining the results from the flow table and slump tests with the information acquired regarding the quality observed by the mortars in the extruded samples, it was possible to define the red lines in Figure 3a as representing the limit of the flow table and slump tests between suitable and unsuitable compositions for 3DP.

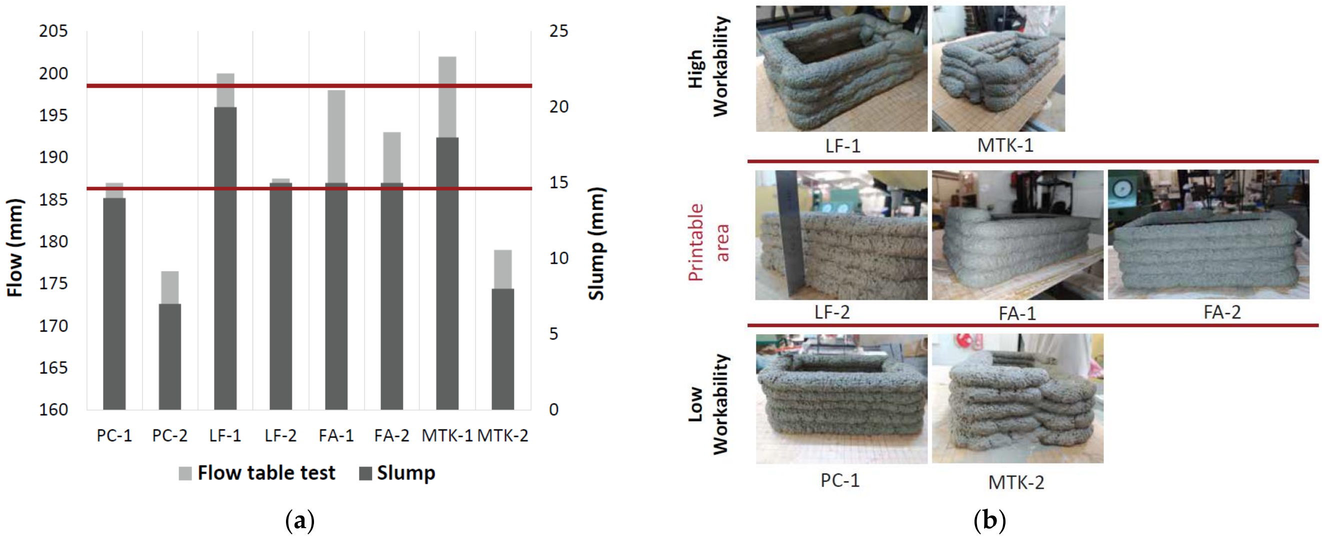

Figure 3. Results of all tests performed: (**a**) flow table and slump tests, and (**b**) extruded samples. The red lines limit acceptable workability for a 3DPM.

4. Discussion

The water-to-powder ratio (w/p) showed to be a critical factor in controlling 3DPM fresh properties. As expected, compositions with the same constituents but with a higher w/p ratio showed greater workability than compositions with a lower w/p ratio (Figure 3a).

When adding a different SCM, for instance, the w/p ratio needs to be optimized. Consequently, the mortars presented w/p ratios between 0.38 and 0.43, except those compositions with MTK which need a higher w/p ratio (0.63 and 0.73) to achieve similar results. These values for the water-to-powder ratio are markedly higher than the ones typically found in the literature [11,12,14] because in this work neither plasticizers nor water reducing admixtures used CO_2.

Comparing mortars with the same w/p ratio and different constituents—PC-2 and LF-2, both with a w/p of 0.39—an increase is observed in workability with the replacement of 50 vol% of cement by LF. This replacement in mortar LF-2 improved the workability in 6%. Similarly, when compared the compositions PC-1 and FA-1 (both with a w/p of 0.41), the replacement of 65 vol% of PC by 40% of LF and 25% of FA, also improved the workability in 6%. The influence of the limestone filler and of the fly ash detected in this work agree with the typical one reported in the literature [22,25].

The compositions tested benefited from the inclusion of some SCM; despite some of them not interacting, in the early ages, chemically with PC, their physical presence affects the mortars' microstructure changing their fresh properties. The LF, as it has a lower hardness than clinker, when ground, presents a greater granulometric distribution that can improve the workability, density and cohesion of the mortar [37,38]. The fine grains fill the gaps between constituents decreasing the water demand but improving the workability. The FA is an industrial by-product resulting from coal-fired power plants; physically they are spherical in shape and smaller than PC and LF. The use of materials with different particle sizes reduces the gaps between the paste and the aggregates, improving the cohesion, stability and surface finish of the mortar. These improvements are visible in compositions FA-1 and FA-2 (with three different SCM). The FA spherical shape and its smaller size result in a better packing of the particles, acting as lubricants, which can be responsible for the increase in the mortars' workability when compared to the other printable composition (LF-2) [30].

When adding metakaolin in MTK-2, even reaching 3DP properties, the high content of water resulted in exudation, as can be seen in Figure 3b, which could result in segregation when hardened. Therefore, this type of SCM had to be included in very small quantities in the mortar's composition. As previously mentioned, in this work chemical admixtures such as superplasticizers were not used, however, as typically found in the literature of mortars with MTK [22,25], using superplasticizers to lower the w/p ratio to optimize the mortar is recommended.

It was also observed that the PC-1 mortar, despite presenting a flow table result between the limits and a capacity to be extruded into layers without major deformations, was dried creating a sample with numerous voids. Thus, it was concluded that the material has buildability and shape retention but bad extrudability due to the lack of workability. This lack of workability can result in filament disruption during extrusion, as demonstrated by Ma et al. [16] and Kazemian et al. [11]. The PC-1 mortar could be optimized for 3DP without the inclusion of any SCM by increasing the w/p ratio, however, the PC consumption would remain too high.

Finally, it was observed that the slump test showed that all mortars in the printable area had 15 mm values, which can be a reference value to define mortars with buildability and shape retention suitable for 3DP [24]. In the flow table tests, the compositions over the limits with too much workability did not allow the layer deposition without deformations, which also happened in study [16].

5. Conclusions

The main challenge of 3DP is to lower the PC consumption of 3DPM. To be printable, the material must have a high paste content, with the inclusion of other powders such as SCM being crucial to achieving 3DP properties and reducing the PC content.

The literature demonstrates that using different SCM combinations can reduce the PC consumption and improve 3DP properties. SCM such as FA and LF are used to improve workability, while others such as MTK, SF and NC are used to improve buildability and shape retention. The combination of SCM with different influences on 3DP properties, for example the combination of FA and SF, has been the most used solution.

The w/p ratio is a very important indicator during the optimization of a 3DPM. Compositions with MTK must be combined with other SCM capable of improving workability and in small quantities, otherwise the amount of water in the composition needs to be increased, which may result in exudation. The combination of PC + LF + FA allowed the reduction of cement from 641 kg/m^3 to 231 kg/m^3 and improved the 3DP properties.

The 3D printing parameters (printing speed, movements, ...) also influence fresh properties, which is a missing factor in this work. Although, the methodology proposed allows anyone without high-tech equipment to start the study in 3DPM, enabling them to characterize constituents for the future development of 3DPM.

Many research centres and universities do not have access to large printers suitable for 3DP on-site due to their high cost. Small printers have been used to test the materials developed in a laboratory environment. Therefore, it is possible to mention that the knowledge of technology is much more advanced for use as a constructive system in prefabrication environments than in on-site 3DP.

Author Contributions: In this section, the role of each author is detailed: J.T., conceptualization, data curation, investigation, writing—original draft; C.O.S., conceptualization, investigation, writing—review and editing; L.M., conceptualization, funding acquisition, investigation, resources, writing—review and editing; B.R., conceptualization, funding acquisition, writing—review and editing; R.N., funding acquisition, resources, writing—review and editing; J.L.A., funding acquisition, resources, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work is financially supported by: Base Funding—UIDB/04708/2020 of the CONSTRUCT—Instituto de I&D em Estruturas e Construções—funded by national funds through the FCT/MCTES (PIDDAC). This work is funded by national funds through FCT—Fundação para a Ciência e a Tecnologia, I.P., under the Scientific Employment Stimulus—Institutional Call—CEECINST/00049/2018. This work is financially supported by Project NORTE-01-0145-FEDER-000022—SciTech—Science and Technology for Competitive and Sustainable Industries, co-financed by Programa Operacional Regional do Norte (NORTE2020), through Fundo Europeu de Desenvolvimento Regional (FEDER); and by Project POCI-01-0145-FEDER-007457—financed by Fundo Europeu de Desenvolvimento Regional through

COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI). CEAU, T2P research group, through FCT project UIDB/00145/2020. João Teixeira would like to thank FCT—Fundação para a Ciência e a Tecnologia, I.P. for PhD grant 2020.07482.BD through FSE/NORTE 2020 funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors are also grateful to INEGI (Instituto de Ciência e Inovação em Engenharia Mecânica e Engenharia Industrial) and LEMC (Laboratório de Ensaio de Materiais de Construção) for all the support and cooperation, as well as to the companies SORGILA, SECIL, Sika and OMYA for the materials supplied.

Conflicts of Interest: The authors declare no conflict of interest.

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