# Development of Plaster Mixtures Formulations for Additive Manufacturing

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## 1 Introduction

For the production of short or even unity series in manufacturing models for processing sanitary ceramics, companies typically use machined polyurethane and epoxy resins. This solution, although efficient, is expensive due the price of these resins that costs approximately 15–20 €/kg, and the waste produced during the machining. These values become more evident with large size/volume pieces, since they require the machining of large quantities of material, high machining time and tooling costs [1].

Thus, it is necessary to find a flexible and economically competitive solution and the production of these moulds or models with gypsum plaster will bring a great reduction in terms of material costs, since the cost of gypsum rounds between 17 and 50 cent/kg. Allied to this lower cost, a big reduction of waste material can be possible too if an additive manufacturing (AM) process is employed, which allows a creation of freeform components with less material to be machined [1].

AM has some disadvantages concerning the surface quality of the parts produced and high initial investment in equipment. Besides that, there is also the problem associated with a production time when compared with conventional processes for machining a piece with the same geometry [2, 3].

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The incorporation of an AM system associated with a machining process, such CNC in the same equipment is currently possible for metallic materials, for example, "INTEGREX i-400 AM" developed by Mazak, associates the process of Laser Metal Deposition (LMD) with a CNC equipment [2].

In addition to equipment for metals, there are several hybrid devices directed to polymers, for example, the "FABTotum" [4], the "ZMorph 2.0S" [5] or the "WASP EVO" [6], where the first one is included in the range of 3D low cost printers.

Although this kind of hybrid equipment for metallic materials or polymers, the use of gypsum in a multi-tasking machine according to the Done-in-one concept [2] is still an unexplored field, and there are some problems associated with the control of extrusion and setting time as well as machining possibilities. The gypsum plaster itself does not fulfil the necessary requirements to be machined in a CNC machine, since it generates significant amounts of dust, and the parts do not have enough mechanical strength to allow the machining of sharp edges. However, it is possible to add certain additives to the gypsum formulations, like binders or plasticizers, in order to improve the resistance to fragmentation of the sharp edges during machining [1].

Summing up, this paper is inserted within an ongoing research project in INEGI which main objective is to create one machine that has the possibility to manufacture high size parts, by AM and the subsequent CNC machining, using non-conventional materials such as gypsum, silica sand or thermosetting resins. Thus, this research work focuses on the study of gypsum plaster formulations able to be used in the new hybrid equipment combining AM and machining.

## 2   Gypsum Properties

Used since ancient times on the form of binder between stone blocks, for example, the pyramids of Egypt, the plaster, extracted from mineral gypsum, is currently a fairly produced worldwide material, having its application expanded to many areas such as construction, medicine, agriculture, artistic sculpture or in the casting process of moulds/models for the sanitary ceramics. The plaster used in this last application is referred as "Plaster of Paris", and is a white, grey or pink powder, essentially consisting of hemihydrate calcium sulphate that is obtained by controlled dehydration of calcium sulphate ($CaSO_4$) hydrate by removal of about 75% of crystallization water. This reaction can be expressed in Eq. (1), where "Q" is the energy provided in the process [7, 8]:

$$CaSO_4 \cdot 2H_2O + Q \rightarrow CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O \qquad (1)$$
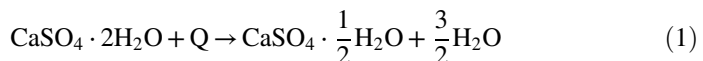
By dehydration it is possible to obtain two types of hemihydrate, the α-hemihydrate and β-hemihydrate plaster, whose difference is mainly due to the method used in their production. The α-hemihydrate is obtained by a wet process

such as autoclaving and β-hemihydrate is obtained under a scarce water vapour process [9].

Concerning hydration, it is possible to reverse de above process passing from one type of hemihydrate, α-hemihydrate or β-hemihydrate, to dihydrate by water addition, expressed in the exothermic reaction (2) [8], that is the focus of this work:

$$CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O + Q \qquad (2)$$
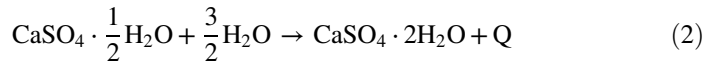
The water reaction with the calcium sulphate hemihydrate forms a slurry which becomes successively more viscous until it hardens completely. This curing time, called "setting time", is usually on the order of 30 min, and varies depending on the type of hemihydrate and consistency of mixture. This setting time is generally lower when using the β-hemihydrate, about 25 min, while the value for α-hemihydrate is approximately 40 min [8, 10].

This hardening is done by meshing of the needles of gypsum crystals during the transition phase, and since the two types of hemihydrates have different setting times, its microstructure will also be slightly different. For the α-hemihydrate, and as a result of a longer setting time, the crystals formed have higher degree of entanglement and interconnection, creating a more consistent and homogeneous structure. On the other hand, as the short β-hemihydrate plaster setting time, the crystals are smaller and stacked, instead of interlocked, as they grow more rapidly at the beginning of hydration, forming shorter and fractured needles, yielding a less consistent and heterogeneous structure [11, 12].

However, the end of setting time of mixtures can be extended to several hours, if retardants are added or reduced to below 3 min if in presence of accelerators [10]. The setting time is the time for complete hardening of the slurry, in other words, when it stops generating heat. Thus, to match the plaster formulations with AM concepts, the use of setting time accelerators is required in order to reduce the extensive time normally associated with de hydration of hemihydrates.

Additives such as potassium sulphate, zinc sulphate or starch are characterized by being a type of chemical accelerator that promotes the formation of sulphate ions [10].

Although these additives reduce the setting time, generally also lead to a reduction of mechanical strength, since in its presence, the crystal morphology of dihydrate will change, giving rise to thinner and shorter needles [9].

Moreover, it is possible to combat this reduction in mechanical strength of plaster formulations using plasticizers. The use of polymers in gypsum formulations leads to an improvement in the mechanical properties. Stav and Bentur [13] have suggested that plaster properties can enhance with incorporation of acrylamide monomers in the inorganic matrix which undergoes polymerization. According to Rubio-Avalos et al. [14], the addition of 10% latex and styrene-butadiene polymer increased the flexural strength of β-hemihydrate from 8.8 MPa to 11.5 MPa.

In short, the addition of superplasticizers contributes to increase flow ability of construction materials such as cement or plaster, for the same ratio water/binder, or allows greater processability for the same water/binder relation. The addition of

0.6% by weight of sulphonated melamine formaldehyde (SMF) led to an increase in compressive and flexural strength by 69% and 42%, respectively, compared to gypsum formulations without any additive, as shown by Pundir et al. [15], and the microstructures obtained are shown on Figs. 1, 2 and 3.
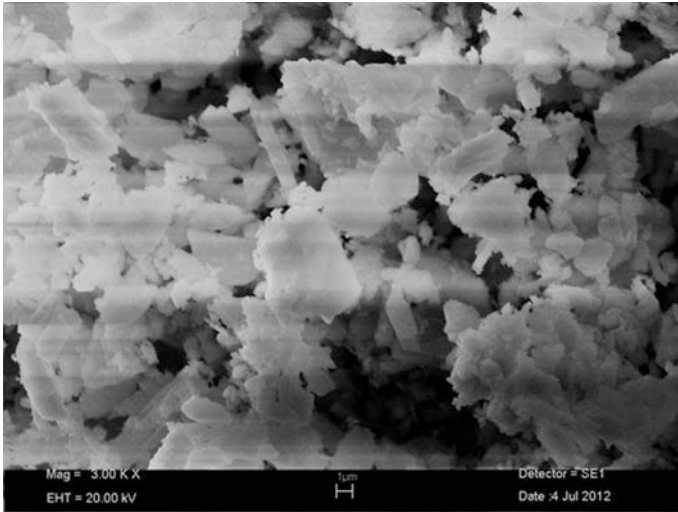
Thus, the above studies, suggest that additives have an important role in the plaster setting time.
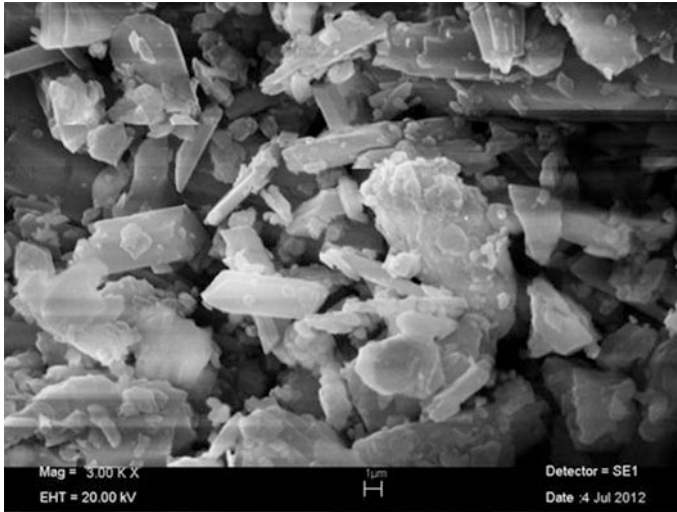


**Fig. 1** Microstructures of β-hemihydrate without superplasticizer [15]
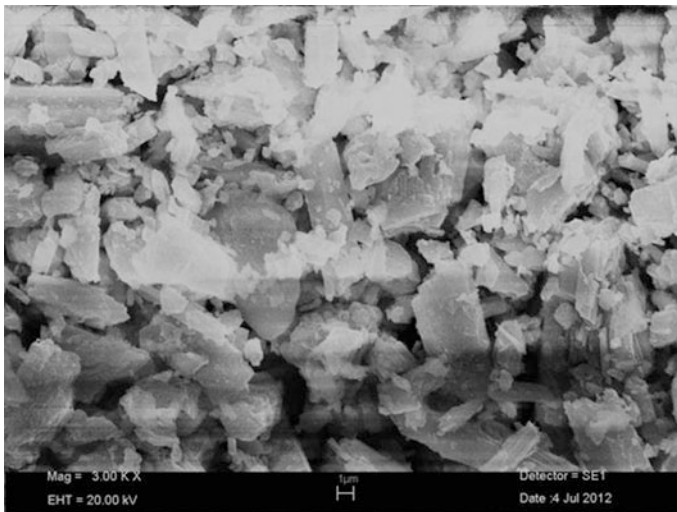


**Fig. 2** Microstructures of β-hemihydrate with 0.4% of superplasticizer (SMF) [15]

**Fig. 3** Microstructures of β-hemihydrate with 0.6% of superplasticizer (SMF) [15]

Different types of additives were selected for α and β gypsum and mixtures formulations to seek for the mixture that can reduce the setting time compatible with AM manufacturing and that simultaneously increases the mechanical strength and machinability of the parts.

# 3 Experimental Work

## 3.1 Materials and Methods

Different additives were selected and purchased. It is important to note that throughout the experimental work distilled water was the liquid media for the slurry mixtures. Table 1 summarizes all additives acquired and the hemihydrates used in the experimental work.

For better analysis of the results, Table 2 shows the more important properties selected from data sheets of the hemihydrates.

Due to the reduced amounts to mix the hemihydrates with the additives and water of each slurry formulation, a Kenwood KM001 mixer was selected.

Initially, for formulations without additives, after adding the water to the hemihydrate, 90 s soak times were used before start mixing during 180 s.

Subsequently, with the addition of accelerators, these times were reduced to 15 s soak and 15 s mixing, due to the fast increase in viscosity.

The slurry produced for each formulation was casted in a silicone (VTX 950) mould with $170 \times 50 \times 50$ mm.

**Table 1** Materials and suppliers

| Material type | Designation | Chemical formula | Commercial name | Supplier | City, Country |
|---|---|---|---|---|---|
| Accelerator | Potassium sulphate | $K_2SO_4$ | – | VWR International—Material de Laboratório, Lda | Camaxide, Portugal |
| Accelerator | Zinc sulfate heptahydrate | $Zn_2SO_4 \cdot 7H_2O$ | – | VWR International—Material de Laboratório, Lda | Camaxide, Portugal |
| Accelerator | Aluminum sulfate | $Al_2(SO_4)_3$ | – | SPD—Sociedade Portuense de Drogas, S.A. | Gondomar, Portugal |
| Accelerator | Sodium sulphate | $Na_2SO_4$ | – | SPD—Sociedade Portuense de Drogas, S.A. | Gondomar, Portugal |
| Accelerator | Calcium chloride | $CaCl_2$ | – | SPD—Sociedade Portuense de Drogas, S.A. | Gondomar, Portugal |
| Accelerator | Calcium chloride anhydrous | $CaCl_2$ | – | VWR International—Material de Laboratório, Lda | Camaxide, Portugal |
| Accelerator | Calcium nitrate tetrahydrate | $Ca(NO_3)_2 \cdot 4H_2O$ | – | VWR International—Material de Laboratório, Lda | Camaxide, Portugal |
| Accelerator | Calcium carbonate | $CaCO_3$ | – | Carban | Leiria, Portugal |
| Accelerator | Polyethylene glycol | | Polietilenoglicol 400 | VWR International—Material de Laboratório, Lda | Camaxide, Portugal |
| Accelerator | Polyvinyl alcohol | – | PVA | INEGI | Porto, Portugal |
| Retarder | Citric acid | – | | SPD—Sociedade Portuense de Drogas, S.A. | Gondomar, Portugal |
| Retarder | Tartaric acid | – | | SPD—Sociedade Portuense de Drogas, S.A. | Gondomar, Portugal |
| Binder | Homopolymer of vinyl acetate | – | Polidisp DV | Resiquímica, S.A. | Porto, Portugal |
| Binder | Styrene-Acrylic Copolymer | – | Polidisp 6660 | Resiquímica, S.A. | Porto, Portugal |
| Binder | Acrylic Copolymers | – | Polidisp 7778 | Resiquímica, S.A. | Porto, Portugal |
| Binder | Copolymers of Acrylic-Veova | – | Polidisp 9957 | Resiquímica, S.A. | Porto, Portugal |

(continued)

**Table 1** (continued)

| Material type | Designation | Chemical formula | Commercial name | Supplier | City, Country |
|---|---|---|---|---|---|
| Binder | Copolymer of Vinyl Acetate—VeoVa | – | Polidisp 7252 | Resiquímica, S.A. | Porto, Portugal |
| Thickener | Methylcellulose | | Methocel\® A4C | VWR International—Material de Laboratório, Lda | Camaxide, Portugal |
| Thickener | Hydroxyethyl methyl cellulose | | Walocel MKX 70000 PP 40 | DOW wolff cellulosics | Bomlitz, Germany |
| Wetting Agent | Propylene Glycol | – | – | AMRESCO | Ohio, USA |
| Wetting Agent | Propylene Glycol | – | – | SPD—Sociedade Portuense de Drogas, S.A. | Gondomar, Portugal |
| Gypsum | β-hemihydrate | $CaSO_4 \cdot 0,5H_2O$ | Gesso Cerâmico Extra | SIVAL | Leiria, Portugal |
| Gypsum | α-hemihydrate | $CaSO_4 \cdot 0,5H_2O$ | Primopor | SIVAL | Leiria, Portugal |

**Table 2** Proprieties of acquired plasters (SIVAL's technical sheet)

| Product | Gypsum—Primopor (SIVAL) | Gypsum—Cerâmico Extra (SIVAL) |
|---|---|---|
| State | α Solid (powder) | β Solid (powder) |
| Colour | White, light beige | White |
| Liquid solution pH @ 20 °C | 6.0–8.0 | 6.0–7.0 |
| Density (g/cm$^3$) | 2.75 | – |
| Apparent density of the powder (g/cm$^3$) | – | 0.6–0.7 |
| Initial setting time (min.) | 21 ± 2 | 12 ± 3 |
| Ending setting time (min.) | – | 28 ± 5 |
| Flexural strength (MPa) | – | ≈ 4.8 |
| Compression strength (MPa) | 125–135 | – |
| Linear expansion (%) | <0.19 | Max. 0.20 |
| Gypsum/Water ratio (kg/dm$^3$) | 2.70–2.90 | 1.25–1.40 |
| Residues—300 μm sieve (%) | – | ≤ 0.008 |
| Residues—150 μm sieve (%) | – | ≤ 0.13 |
| Residues—45 μm sieve (%) | – | ≤ 2.3 |

To determine the setting time temperature (maximum temperature reached during the hardening), a type K thermocouple was placed in the centre of the mould, as shown in Fig. 4.

The samples for mechanical testing, 3 specimens of 160 × 40 × 40 mm, were cast in the silicone mould of Fig. 5.

The flexural strength tests were conducted in accomplishment to BS EN 12859: 2011. Three specimens (Fig. 6) of each formulation were dried until the mass was constant (a constant mass is set when 2 successive weighing's, 24 h apart, differ by less than 0.1%).

The 3 point bend tests were performed in an Instron 4208 machine (Fig. 7), with a 100 kN load cell, applied on the centre of the specimens that were supported in two points with 100 mm span and a feed rate defined by ASTM 647-88: 2004, of 1 mm/min.

The fractured surfaces were analysed to check the porosity, mixture heterogeneities and other defects that can affect the modulus of rupture.

For all formulations, the accelerators, binders or water are expressed in weight percentages relative to the amount of gypsum. The water percentage was selected to allow a homogeneous mixture and fluidity for casting into the moulds.



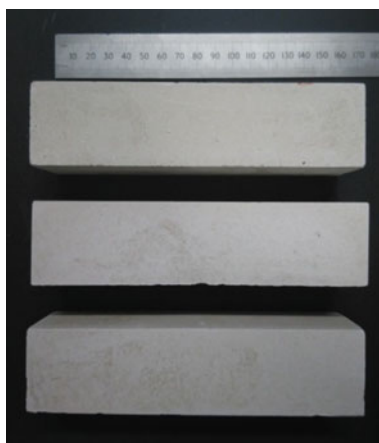**Fig. 4** Silicon mould for determining the setting time temperature
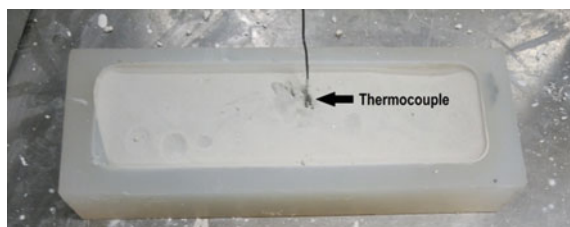
**Fig. 5** Silicon mould for production of samples for 3 point bending test



**Fig. 6** Test specimens for 3 point bending test



**Fig. 7** Instron 4208 testing equipment

**Fig. 8** Poor quality samples



During the experimental process, it was possible to analyse the behaviour of mixtures with various additives, and thus, a set of 21 additives and 2 types of hemihydrates, in a total of 130 examined formulations were selected. The selected additives were: potassium sulphate, zinc sulphate, sodium sulphate, calcium carbonate and calcium chloride as accelerators, polidisp 7252, polidisp DV, polidisp 6660 and polidisp 7778 as binders and methocel A4C as thickener.

Due to adversities presented by some formulations, the results with no practical interest, either by the slurry hardened too quickly, heterogeneous mixture or inappropriate amount of bubbles, were excluded. Some of these defects are shown in Figs. 8, 9 and 10.

**Fig. 9** Sample with lumps and pores
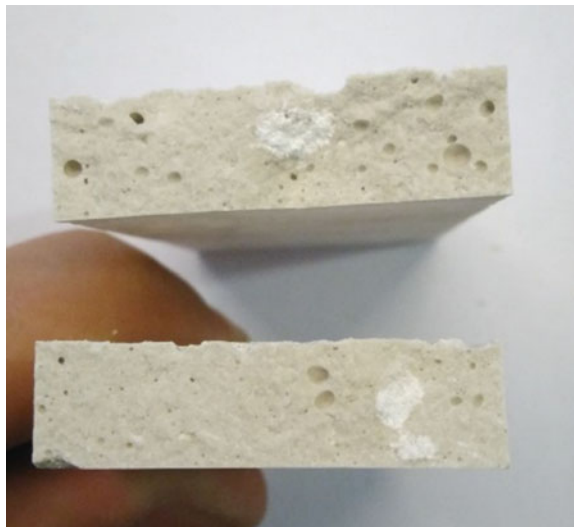
**Fig. 10** Samples with abundant pores

The tested formulations and the results obtained for the bending tests are presented in the following chapter. However, in this paper, only the most interesting mixtures are analysed, which means only two accelerators and two binders.

## 4 Results

This chapter presents and compares the values from the tests for three "families" of formulations; formulations without additives, formulations with accelerator and formulations with accelerator and binder.

The additives used for comparison are:

- Potassium sulfate ($K_2SO_4$)—Accelerator
- Calcium carbonate ($CaCO_3$)—Accelerator
- Copolymer of Vinyl Acetate—VeoVa (Polidisp 7252)—Binder
- Acrylic Copolymers (Polidisp 7778)—Binder

### 4.1 Slurries Temperature Evolution

The Fig. 11 shows the curves for a formulation of each of the "families" of α-hemihydrate formulations and represents the evolution of the temperature inside the slurry during the setting time.

Figure 11 shows that the addition of potassium sulphate leads to a faster temperature increase, reducing the setting time from 45 to 25 min, which represents a reduction of 44%. The addition of Polidisp 7252 delays slightly the speed, reaching
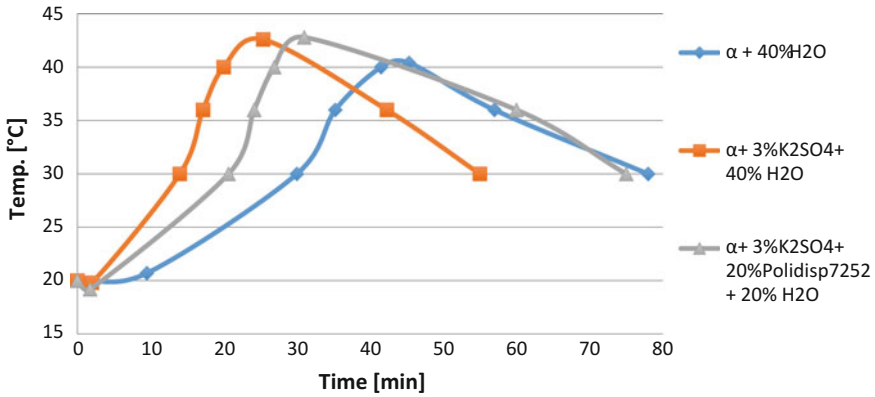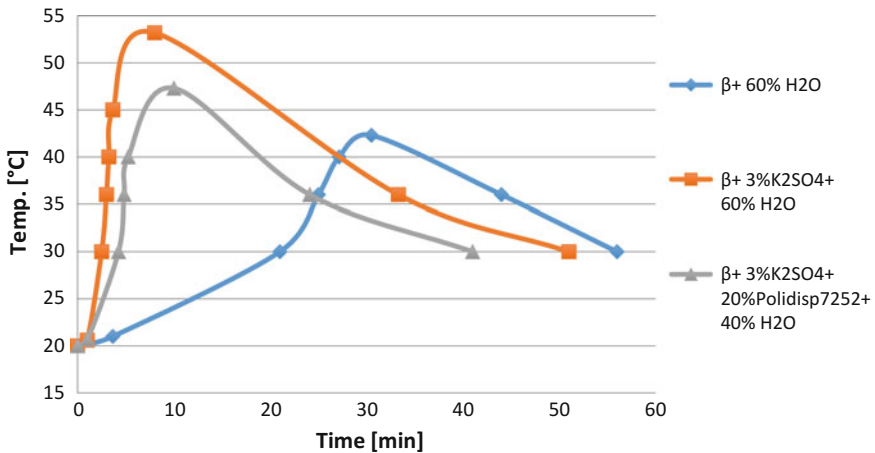
**Fig. 11** Temperature evolution as a function of the setting time of gypsum α-hemihydrate

the peak temperature at 31 min, however it still is 14 min faster than the formulation without additives.

Pure β-hemihydrate gypsum setting time is shorter than α-hemihydrate gypsum, and a reduction of 72% (29 to 8 min) can be obtained with the accelerator, as shown in Fig. 12.

Formulation with 50% α-hemihydrate and 50% β-hemihydrate (Fig. 13) have the same tendency has the previous formulations, however with different setting time.



**Fig. 12** Temperature evolution according to the setting time for β-hemihydrate gypsum
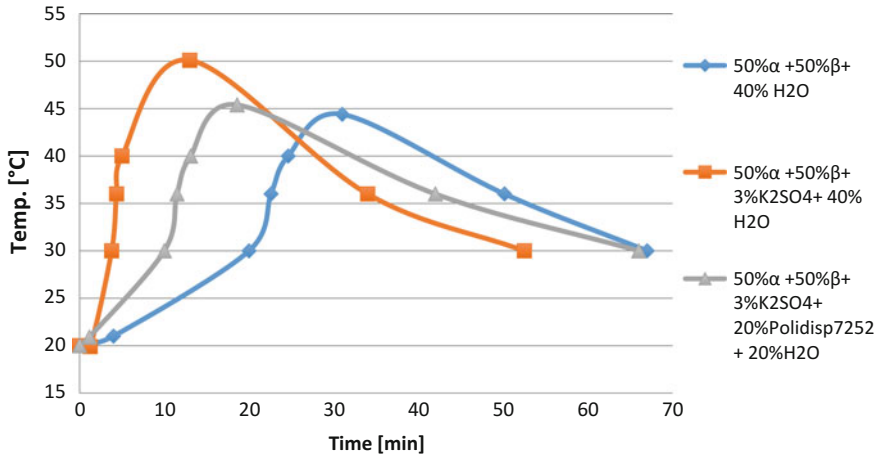
**Fig. 13** Temperature evolution as a function of setting time for α-hemihydrate + β-hemihydrate formulation

The results obtained for the three types of formulations show that the setting time is reduced when $K_2SO_4$ accelerator is introduced in the mixture. Although binder, introduced to increase the mechanical strength of the plaster, has an opposite effect of the accelerator, the setting time is still lower than the one obtained with the pure raw material, which is promising for the combined manufacture process to be implemented.

## 4.2 Flexural Strength

Figure 14 presents the modulus of rupture and the respective setting time of the various formulations.

In general, the addition of potassium sulphate to gypsum formulations led to a reduction of the setting time of about 45% for the α-hemihydrate gypsum, 74% for β-hemihydrate gypsum and 58% for α + β, however the modulus of rupture is also reduced. This effect in β-hemihydrate is not so notorious.

The combination of an accelerator and a binder, although increasing the setting time, relative to the mixture with only an accelerator, retrieves the lost resistance promoted by the accelerator.

Compared to formulations without additives, the formulations with additives that performed better matching between setting time and flexural strength were the formulations with calcium carbonate ($CaCO_3$) and acrylic copolymer (Polidisp 7778). Regarding formulations with α-hemihydrate, there was a reduction of about
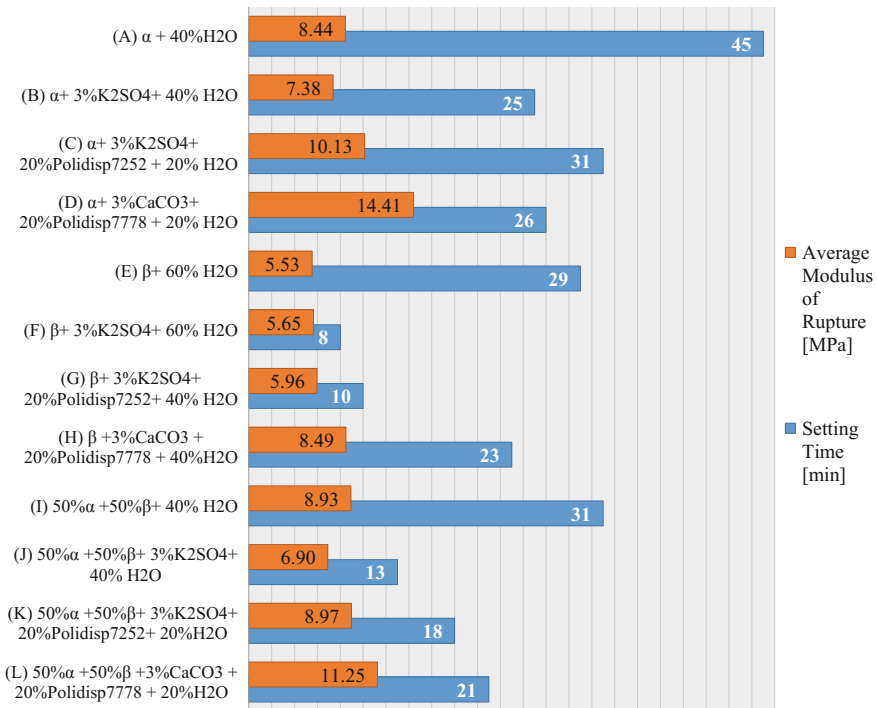
**Fig. 14** Comparison of setting times and modulus of rupture from the various formulations

42% of setting time, and a 71% increase in the value of average modulus of rupture (one of the tested samples showed a modulus of rupture value of about 15.48 MPa, which represents a gain of 83%).

For β-hemihydrate with CaCO3 and Polidisp 7778, a 20% reduction in setting time and an increase of 53.5% of modulus of rupture was obtained. For 50% α + 50% β with CaCO$_3$ and Polidisp 7778, promote a 32% reduction in the setting time, and a 26% increase in the average modulus of rupture.

Tables 3, 4 and 5, present the results obtained in 3 point bending with α-hemihydrate, β-hemihydrate and 50% α + 50% β-hemihydrate, respectively.

- It is important to note that in these tables:
- The percentage is always 3% for accelerator and 20% for binder.
- For α-hemihydrate and α + β tables, the percentage of added water is 40% if there is no binder in the formulation and 20% with binder in the formulation.
- For β-hemihydrate table, the percentage of added water is 60% if there is no binder in the formulation and 40% with binder in the formulation.

**Table 3** Results for 3 point bending test for α-hemihydrate formulations

| # | Formulation | | Weight (g) | Max. force (N) | Mr (modulus of rupture) (MPa) | Average Mr (MPa) |
|---|---|---|---|---|---|---|
| 1 | α | A | 384.4 | 3503 | 8.18 | 8.44 |
| | | B | 384.4 | 3345 | 8.03 | |
| | | C | 385.8 | 3874 | 9.11 | |
| 2 | α + K$_2$SO$_4$ | A | 393.3 | 3263 | 7.28 | 7.38 |
| | | B | 396.6 | 3496 | 7.67 | |
| | | C | 393.4 | 3234 | 7.18 | |
| 3 | α + Zn$_2$SO$_4$ | A | 395.5 | 4458 | 10.04 | 9.84 |
| | | B | 397.8 | 4273 | 9.70 | |
| | | C | 395.2 | 4350 | 9.77 | |
| 4 | α + Na$_2$SO$_4$ | A | 397 | 2367 | 5.33 | 4.81 |
| | | B | 388.5 | 1756 | 3.98 | |
| | | C | 394.5 | 2282 | 5.12 | |
| 5 | α + CaCl$_2$ | A | 391.2 | 1992 | 4.99 | 4.90 |
| | | B | 381.2 | 1979 | 4.97 | |
| | | C | 382.9 | 1895 | 4.74 | |
| 6 | α + CaCO$_3$ | A | 387.6 | 2617 | 5.84 | 6.59 |
| | | B | 392 | 2846 | 6.47 | |
| | | C | 386.7 | 3305 | 7.45 | |
| 7 | α + K$_2$SO$_4$ + Polidisp7252 + Antifoam | A | 432.5 | 4669 | 10.45 | 10.13 |
| | | B | 429.9 | 4167 | 9.23 | |
| | | C | 431.5 | 4810 | 10.72 | |
| 8 | α + Zn$_2$SO$_4$ + Polidisp7252 + Antifoam | A | 428.6 | 3659 | 8.14 | 7.55 |
| | | B | 428.8 | 3291 | 7.29 | |
| | | C | 427.2 | 3259 | 7.22 | |
| 9 | α + CaCO$_3$ + Polidisp7252 + Antifoam | A | 432.3 | 4384 | 9.89 | 10.20 |
| | | B | 431 | 4234 | 9.56 | |
| | | C | 432.5 | 5023 | 11.16 | |
| 10 | α + Zn$_2$SO$_4$ + Polidisp DV + Antifoam | A | 412.9 | 2217 | 4.83 | 5.29 |
| | | B | 410.8 | 1997 | 4.50 | |
| | | C | 401.6 | 2937 | 6.52 | |
| 11 | α + CaCO$_3$ + Polidisp DV + Antifoam | A | 423.9 | 3232 | 7.16 | 7.07 |
| | | B | 424 | 3012 | 6.75 | |
| | | C | 425.4 | 3302 | 7.29 | |
| 12 | α + CaCO$_3$ + Polidisp 6660 + Antifoam | A | 409.1 | 6027 | 13.65 | 13.51 |
| | | B | 412.5 | 5860 | 13.29 | |
| | | C | 412.7 | 6003 | 13.57 | |
| 13 | α + CaCO$_3$ + Polidisp 7778 + Antifoam | A | 423.3 | 6875 | 15.48 | 14.41 |
| | | B | 424.3 | 6268 | 14.24 | |
| | | C | 420.5 | 5970 | 13.51 | |
| 14 | α + Methocel | A | 349 | 3281 | 7.41 | 6.90 |
| | | B | 349.6 | 3259 | 7.07 | |
| | | C | 347.3 | 2875 | 6.22 | |

**Table 4** Results for 3 point bending test for β-hemihydrate formulations

| # | Formulation | | Weight (g) | Max. force (N) | Mr (modulus of rupture) (MPa) | Average Mr (MPa) |
|---|---|---|---|---|---|---|
| 15 | β | A | 299.7 | 2465 | 5.62 | 5.53 |
| | | B | 302.6 | 2492 | 5.74 | |
| | | C | 302.6 | 2284 | 5.24 | |
| 16 | β + $K_2SO_4$ | A | 306.2 | 2505 | 5.67 | 5.65 |
| | | B | 305.5 | 2544 | 5.77 | |
| | | C | 305.2 | 2436 | 5.50 | |
| 17 | β + $Zn_2SO_4$ | A | 307 | 1485 | 3.36 | 4.57 |
| | | B | 307 | 2340 | 5.29 | |
| | | C | 306.1 | 2288 | 5.05 | |
| 18 | β + $Na_2SO_4$ | A | 297.7 | 1591 | 3.63 | 3.39 |
| | | B | 302 | 1571 | 3.55 | |
| | | C | 298.9 | 1349 | 3.00 | |
| 19 | β + $CaCl_2$ | A | 308.4 | 1075 | 2.44 | 2.49 |
| | | B | 304.6 | 1200 | 2.73 | |
| | | C | 315.5 | 1024 | 2.31 | |
| 20 | β + $CaCO_3$ | A | 306.5 | 1706 | 3.77 | 3.53 |
| | | B | 312.2 | 1258 | 2.78 | |
| | | C | 305.5 | 1787 | 4.05 | |
| 21 | β + $K_2SO_4$ + Polidisp7252 + Antifoam | A | 328.1 | 2595 | 5.92 | 5.96 |
| | | B | 327.4 | 2568 | 5.80 | |
| | | C | 330.2 | 2715 | 6.17 | |
| 22 | β + $Zn_2SO_4$ + Polidisp7252 + Antifoam | A | 328.6 | 2889 | 6.46 | 7.36 |
| | | B | 327.9 | 3500 | 7.74 | |
| | | C | 328.2 | 3505 | 7.87 | |
| 23 | β + $CaCO_3$ + Polidisp7252 + Antifoam | A | 333.7 | 3998 | 9.05 | 8.30 |
| | | B | 334.1 | 3554 | 7.87 | |
| | | C | 334.4 | 3579 | 7.97 | |
| 24 | β + $K_2SO_4$ + Polidisp DV + Antifoam | A | 302.2 | 2461 | 5.63 | 5.40 |
| | | B | 303.3 | 2276 | 5.20 | |
| | | C | 300.9 | 2382 | 5.38 | |
| 25 | β + $Zn_2SO_4$ + Polidisp DV + Antifoam | A | 306 | 3100 | 6.98 | 6.50 |
| | | B | 309.7 | 2726 | 6.11 | |
| | | C | 307.1 | 2892 | 6.42 | |
| 26 | β + $CaCO_3$ + Polidisp DV + Antifoam | A | 302.2 | 2909 | 6.48 | 6.61 |
| | | B | 299.5 | 3144 | 7.16 | |
| | | C | 305.2 | 2740 | 6.17 | |
| 27 | β + $K_2SO_4$ + Polidisp 6660 + Antifoam | A | 326.3 | 2719 | 6.26 | 6.39 |
| | | B | 324.7 | 2727 | 6.18 | |
| | | C | 326.6 | 2970 | 6.73 | |
| 28 | β + $CaCO_3$ + Polidisp 6660 + Antifoam | A | 322.7 | 2905 | 6.78 | 6.66 |
| | | B | 324.7 | 2905 | 6.80 | |
| | | C | 324.8 | 2725 | 6.39 | |

(continued)

**Table 4** (continued)

| # | Formulation | | Weight (g) | Max. force (N) | Mr (modulus of rupture) (MPa) | Average Mr (MPa) |
|---|---|---|---|---|---|---|
| 29 | β + K$_2$SO$_4$ + Polidisp 7778 + Antifoam | A | 327.2 | 3356 | 7.58 | 8.24 |
| | | B | 325.1 | 3881 | 8.82 | |
| | | C | 326.1 | 3644 | 8.30 | |
| 30 | β + CaCO$_3$ + Polidisp 7778 + Antifoam | A | 321.3 | 3788 | 8.60 | 8.49 |
| | | B | 322.9 | 3785 | 8.59 | |
| | | C | 322.8 | 3643 | 8.28 | |
| 31 | β + Methocel | A | 287.3 | 2358 | 5.26 | 4.69 |
| | | B | 288.5 | 1626 | 3.62 | |
| | | C | 289.8 | 2368 | 5.18 | |

## *4.3 Fracture Sections of Specimens After 3 Point Bending Test*

Comparing the fractured surface sections (40 × 40 mm) of α plaster crystals formulations with β and α + β ones, it is possible to register that pure α-hemihydrate formulations have less occurrence of pores. This is related with the fact that, growing more slowly (higher setting time), allow air bubbles to be released, contributing to more compact formulations that in general have higher flexural strength (see tables above).

The α plaster mixtures containing Polidisp (either 7252 or 7778) acquire a higher viscosity in a shorter period, leading to higher air bubbles entrapment into the slurry, as can be seen in Fig. 15. Figures 16 and 17 show β and α + β sections, where higher amount of porosity can be observed.

The generation of pores (amount and diameter) in the periphery has greater consequence in flexural strength reduction because it is in this region that the specimen is under greater tensile stresses.

Figure 18 shows the fracture of the specimens which formulation had a better flexural strength.

Figure 18a is related to the sample of α plaster formulation and reached a 15.48 MPa modulus of rupture, Fig. 18b is relative to β plaster with a 8.6 MPa and Fig. 18c of α + β with a 14.54 MPa. As CaCO$_3$ is less effective than K$_2$SO$_4$ with regard to accelerating the crystallization reaction, i.e., reducing the setting time of the slurry, formulations with this accelerator become more favourable in realising the bubbles introduced during the slurry mixture.

The good flexural strength results for formulations with Polidisp 7778, an acrylic-based binder, is an indicator that this kind of binder is preferred instead of a binder based on vinyl acetate—VeoVa, as Polidisp 7252.

**Table 5** Results for 3 point bending test for $\alpha + \beta$ formulations

| # | Formulation | | Weight (g) | Max. Force (N) | Mr (modulus of rupture) (MPa) | Average Mr (MPa) |
|---|---|---|---|---|---|---|
| 32 | $\alpha + \beta$ | A | 386 | 3351 | 7.51 | 8.93 |
| | | B | 389 | 4026 | 8.89 | |
| | | C | 388.4 | 4661 | 10.41 | |
| 33 | $\alpha + \beta + K_2SO_4$ | A | 386.6 | 3737 | 8.47 | 6.90 |
| | | B | 383.6 | 2464 | 5.61 | |
| | | C | 391 | 2936 | 6.61 | |
| 34 | $\alpha + \beta + Zn_2SO_4$ | A | 379.9 | 4080 | 9.20 | 8.17 |
| | | B | 381.3 | 3606 | 8.04 | |
| | | C | 379.6 | 3260 | 7.27 | |
| 35 | $\alpha + \beta + Na_2SO_4$ | A | 386.7 | 2242 | 5.10 | 5.44 |
| | | B | 384.9 | 2171 | 4.92 | |
| | | C | 385.6 | 2853 | 6.29 | |
| 36 | $\alpha + \beta + CaCO_3$ | A | 386 | 3640 | 8.33 | 7.99 |
| | | B | 384.9 | 3094 | 7.05 | |
| | | C | 384.2 | 3766 | 8.59 | |
| 37 | $\alpha + \beta + K_2SO_4 + $ Polidisp7252 + Antifoam | A | 411.1 | 3621 | 8.33 | 8.97 |
| | | B | 410.6 | 3941 | 9.14 | |
| | | C | 411.4 | 4059 | 9.44 | |
| 38 | $\alpha + \beta + Zn_2SO_4 + $ Polidisp7252 + Antifoam | A | 421.7 | 3782 | 8.44 | 7.56 |
| | | B | 425 | 3139 | 6.99 | |
| | | C | 424.6 | 3178 | 7.26 | |
| 39 | $\alpha + \beta + CaCO_3 + $ Polidisp7252 + Antifoam | A | 405.5 | 4499 | 10.06 | 10.25 |
| | | B | 413.4 | 4969 | 10.77 | |
| | | C | 412.6 | 4513 | 9.92 | |
| 40 | $\alpha + \beta + K_2SO_4 + $ Polidisp DV + Antifoam | A | 388.3 | 1828 | 4.24 | 3.76 |
| | | B | 388.6 | 1659 | 3.80 | |
| | | C | 389.5 | 1455 | 3.22 | |
| 41 | $\alpha + \beta + Zn_2SO_4 + $ Polidisp DV + Antifoam | A | 385.2 | 3820 | 8.24 | 7.92 |
| | | B | 385.1 | 3893 | 8.34 | |
| | | C | 384.8 | 3329 | 7.19 | |
| 42 | $\alpha + \beta + CaCO_3 + $ Polidisp DV + Antifoam | A | 400.2 | 2212 | 4.89 | 4.64 |
| | | B | 400.9 | 1901 | 4.29 | |
| | | C | 403.4 | 2134 | 4.74 | |
| 43 | $\alpha + \beta + K_2SO_4 + $ Polidisp 6660 + Antifoam | A | 410.2 | 5560 | 12.50 | 12.72 |
| | | B | 412.5 | 5764 | 12.66 | |
| | | C | 411.5 | 5769 | 13.00 | |
| 44 | $\alpha + \beta + CaCO_3 + $ Polidisp 6660 + Antifoam | A | 404.2 | 6118 | 13.71 | 13.74 |
| | | B | 406.3 | 5860 | 13.09 | |
| | | C | 401.2 | 6365 | 14.43 | |
| 45 | $\alpha + \beta + K_2SO_4 + $ Polidisp 7778 + Antifoam | A | 400.6 | 6035 | 13.73 | 13.53 |
| | | B | 400.1 | 5820 | 13.30 | |
| | | C | 400.2 | 5911 | 13.55 | |
| 46 | $\alpha + \beta + CaCO_3 + $ Polidisp 7778 + Antifoam | A | 402.6 | 4852 | 10.74 | 11.25 |
| | | B | 400.4 | 6526 | 14.54 | |
| | | C | 397.1 | 3750 | 8.46 | |
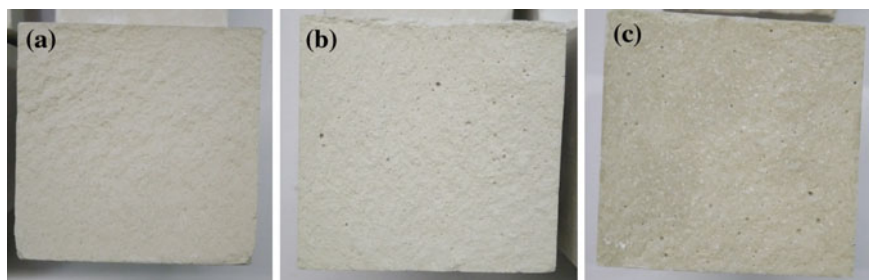
**Fig. 15** Fracture surface of the tested specimens of gypsum α-hemihydrate formulations; **a** pure gypsum; **b** α + K$_2$SO$_4$; **c** α + K$_2$SO$_4$ + Polidisp 7252
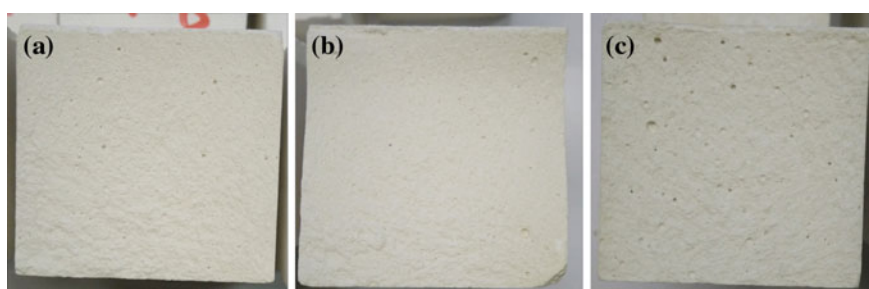


**Fig. 16** Fracture surface of the tested specimens of gypsum β-hemihydrate formulations; **a** pure gypsum β; **b** β + K$_2$SO$_4$; **c** β + K$_2$SO$_4$ + Polidisp 7252
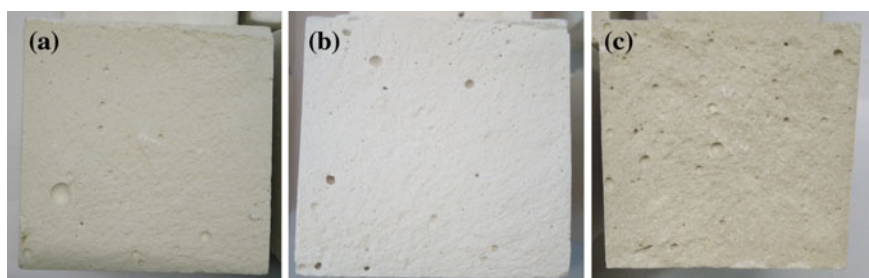


**Fig. 17** Fracture surface of the test specimens of gypsum α + β formulations; **a** α + β; **b** α + β + K$_2$SO$_4$; **c** α + β + K$_2$SO$_4$ + Polidisp 7252
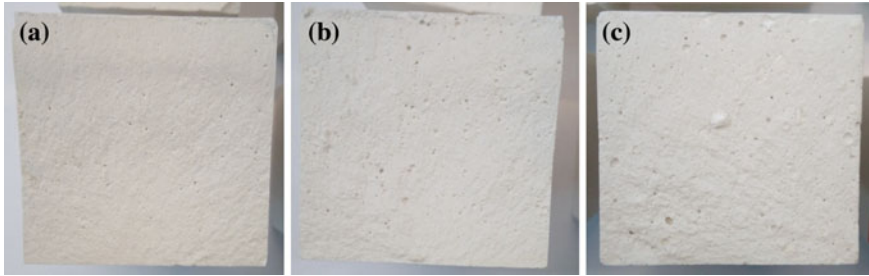
**Fig. 18** Fracture surface of the test specimens of gypsum + CaCO₃ + Polidisp 7778 formulations; **a** α + CaCO₃ + Polidisp 7778; **b** β + CaCO₃ + Polidisp 7778; **c** α + β + CaCO₃ + Polidisp 7778

## 5 Conclusion and Future Work

With this study it was possible to produce some exploratory formulations capable of being processed by a hybrid equipment composed by Additive Manufacturing and Machining processes. Tailoring the slurry viscosity to be deposited in successive layers without the occurrence of flow and achieve mechanical properties with enough resistance to sharp edges fragmentation during machining, seems to be a promising step to be able to produce low cost models and moulds with good surface finishing.

The fast reduction in the setting time and thus the rapid increase in slurry viscosity obstructs the release of air bubbles generated during the mixing of the components, thereby causing pores in the final parts that decrease the mechanical strength of the plaster. Thus, it is advisable that in the future the plaster mixture with liquid is performed under vacuum and that the extrusion is done in a way to avoid porosity.

The increase in setting time with an accelerator and a binder in the formulation with CaCO₃ and Polidisp 7778 allows the reduction of the setting time by 42, 20 and 32% for formulations with α-hemihydrate, β-hemihydrate and plaster α + -hemihydrate, respectively, when compared to the corresponding formulations without additives.

Regarding the flexural strength, the addition of the accelerator CaCO₃ and Polidisp 7778 binder led to an increase in the average modulus of rupture of 71, 53 and 26% for formulations with α-hemihydrate, β-hemihydrate and plaster α + -hemihydrate, respectively, compared to the respective formulations without additives.

Considering the results of this study, the next objective is making extruding tests of these slurries pastes in order to control the fluidity and thixotropy, and perform adhesion tests between layers of extruded slurries, and do machining tests of gypsum blocks with additives to investigative the surface finishing after machining and analysis of cutting tools wear.

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