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TEMPERATURE PRE-TREATMENT OF GYPSUM FOR POWDER BASED 3D PRINTING TECHNOLOGY

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SUMMARY: In recent years many researchers have been involved in studies in the field of pre-treatment of various raw materials. Temperature treatment of materials results in several advantages, which have been already recognised and successfully applied in various fields of applications. Where at the same time, the practices has been adopted also in the field of 3D printing. Enhanced strength and stiffness, assuring desirable performance criteria of the 3D printed models, reflect the most important characteristics. 3D printing binder jetting technology is based on the application of liquid binders onto powdered material, where gypsum powders have been commercially used as a base raw material. As natural raw materials can be replaced by other materials, such as recycled industrial by products, the aim of this research work was to evaluate the potential usage of three synthetic gypsum powders from different industrial processes for 3D printing. The investigation covered (a) mineralogical and microstructural characteristics of gypsums from different origin and (b) the effect of pre-treatment of gypsum powders at different temperatures (up to 500 °C). On the basis of the results, the most promising temperature regime for each different waste gypsum powder treatment, reflecting in the most optimal setting time, was defined. Synthetic gypsums were characterized by X-ray diffraction (QXRD), scanning electron microscopy (SEM) and differential thermal analysis (TG/DTA). The results showed that all three synthetic gypsums (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$) thermally degrade into calcium sulfate anhydrite ($CaSO_4$) via an intermediate calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$, bassanite) phase. Microstructural and mineralogical differences were observed when temperature treated gypsums from different origins were compared. The detailed knowledge of gypsum powder properties at different temperature regime is important parameter for the assurance of 3D printing key parameters such as flowability, roughness and wettability, especially for determination of saturation levels and setting time. After all, these parameters define final mechanical properties of 3D printed structures. By using such approach, the understanding of material compatibility for 3D printing technology can be defined and improved if necessary.

KEY WORDS: synthetic gypsum, 3D printing, binder jetting, pre-treatment, temperature.

1 INTRODUCTION

3D printing or additive manufacturing is well-known technology, usable in different fields of application, distinguished in terms of their approach to joining the layers [1]. Products are made by means of specialized digital geometric models, using layer-by-layer technology, where different binders form solid objects with defined properties. One of the seven generic groups is binder jetting technology, which is based on the application of liquid binders onto particles of “gypsum like” powder base material [1]. To improve environmental awareness and achieve an economically viable solution, **synthetic gypsum** as industrial by-product, can be used **to replace commercially available powders in 3D printing**.

Synthetic gypsum is generated in vast quantities, but its disposal is an ongoing issue. In order to achieve the efficient recycling of synthetic gypsum a long-term strategy is vitally needed [2]. Its **recycling** leads to socioeconomic and environmental benefits and is already used in several applications, such as in cement production [2,3], as material for soil stabilization [4], as building material and binder [5], as asphaltic bitumen modifier and as material for road pavement [6,7]. Recently, only few researchers have investigated recycling materials for their usage in 3D printing [8,9]. To the best of the author’s knowledge, no cases of application of the waste gypsum as a raw material for 3D printing are described in the literature. It should be noted that such powders should have comparable characteristics to conventional ones. To achieve such properties, some pre-treatment processes are usually applied.

Research in the field of **pre-treatment** of various raw materials have been broadly engaged in last year's [10,11] using different processes (kiln residence time, high and low temperatures) [2,12], focused on converting gypsum to hemihydrate or anhydrite. Calcium sulphate dihydrate (gypsum) starts to convert at temperatures less than 200°C into two different modifications of calcium sulphate hemihydrate (basanite): α-hemihydrate and β-hemihydrate. The α-hemihydrate is obtained at temperatures between 120 – 160 °C with a hydrothermal reaction at high pressures (up to 8 bar) which demands a more complex production process [2]. The α-hemihydrate is applied in applications where higher strengths of the products are expected (e.g. sculptures) [2]. β-hemihydrate is obtained at temperatures between 120 – 180 °C through the dry calcination of gypsum which is more economical process. The β-hemihydrate is commonly applied in applications as a binding material in civil construction (e.g., plasterboard production) [2,13,14,15].

In order to systematically define the **calcination mechanism**, Liu et. al. [16] evaluated phosphogypsum calcination treatment at the temperature of 150 °C, 350 °C, 600 °C and 800 °C with calcination time of 0.5 h, 1 h, 1.5 h and 2 h. The modification effect varied with calcination temperature and calcination time. The results have shown that 90% of the setting time was shortened after calcination temperature of 350 °C for 2 h. Bumanis et al. [17] researched calcination of phosphogypsum at temperatures of 100 °C, 120°C, 140 °C, 160 °C and 180 °C for 4 h to obtain a binder material. The results have shown that higher heat temperature treatment of phosphogypsum reduces time of decomposition of phosphogypsum to hemihydrate and slightly increase the initial setting time of obtained binder. Another conclusion was that the increase of heat temperature from 120 °C to 180 °C did not improve the final compressive strength of the pastes. Koper [11] investigated four different temperatures ranging from 170 to 190 °C (samples with a constant water to gypsum ratio of w/g = 0.75). It was noted that the calcination temperature influenced the setting time of the gypsum. As concluded by Rossetto et. al. [18], the gypsum setting can be described as a physical phenomenon where gypsum crystal nuclei are formed, so dihydrate crystals start precipitating, increasing the consistency of the paste (initial setting time). With the increase in the rate of hydration reaction the paste attains sufficient hardness to support stress (final setting time). The gain of strength is defined as hardening. Recently, knowledge has progressed in the field of 3D printing, reflecting the enhancement in the strength and stiffness of the 3D printed models which meet their performance criteria.

Present research is focused on evaluation of the influence of calcination conditions (temperature) of different gypsums powders on setting time. This parameter is crucial in 3D printing technology. Different analytical techniques were used to characterize calcined gypsum powders (e.g., thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM)).

2 MATERIALS AND METHODS

Synthetic gypsum powders used within this work were originated from different industrial processes. The first one originated from flue gas desulfurization process (designated as G1), the second one from acid-neutralizing industrial processes (designated as G2) and the third one from the wastewater treatment process during crystal glass production (designated as 3). Thermal pre-treatment of samples was performed in a laboratory furnace at different temperatures between 40-500 °C for ~5h (150 °C/h and 2h holding). QXRD, TG/DTA and SEM were used for mineral and microstructure characterisation. As a reference, commercial powder Zp151 from the 3DSystems manufacturer was used in Vicat testing.

The thermal **gravimetry and differential thermal analysis (TG/DTA)** measurements were performed using a STA 409 PC Luxx thermal analyser. Powders of 25 mg were used and analysed in the Al_2O_3 crucibles in the temperature range of 25 to 600 °C with heating rate of 10 K/min in the atmosphere of synthetic air 5.0 was used.

The phase composition was defined by quantitative **X-ray diffraction analysis (QXRD)**, using an Empyrean (PANalytical, Netherlands) diffractometer with Cu-Kα radiation and Rietveld refinement procedure. Powder diffraction data were collected at a tube tension of 40 kV and a tube current of 45 mA using a 2θ step size of 0.01° and measurement time of 100 s per step. The results were analyzed by Highscore (PANalytical, Netherlands) diffraction software, using the Powder Diffraction File PDF-4+ (ICDD, USA) database as the reference source of data. The data was collected at ambient temperature in a range from 5 to 70° (2θ). For the quantification of gypsum, basanite and anhydrite, the ICSD collection codes 2057, 69060 and 16382 respectively, was used.

Morphology and microstructure were investigated, by means of a scanning electron microscope (SEM, JEOL JSM IT500, Japan), equipped with energy dispersive spectroscopy (EDS, Oxford instruments, UK). The SEM/EDS analyses

were performed in low-vacuum mode with a chamber pressure of 90 - 100 Pa, and an accelerating voltage of 15- 20 kV. These analyses were performed on raw samples.

Setting time of gypsum powders were tested by Vicat consistency needle penetration method, following the standard SIST EN 196-3:2017 [19]. Water binder ratio was 0.62, where the needle was indented into paste with the interval off 1 min. All powders used in this testing have the same granulation, 48 % were <45 µm, 31 % in the range between 45-63 µm and 21 % in the range between 63-90 µm.

3 RESULTS

3.1 Thermal behaviour of synthetic gypsums

The results of the TG-DTG analysis are presented in Fig. 1. The TG curves shows a total mass loss of all the samples in the temperature range up to 180°C, which corresponds to the loss of structural water. DTA data involves two overlapped processes in the range from 120 to 180°C, assigned to endothermic effect. First major peak at ~150°C is attributed to the partial dehydration of the gypsum to calcium sulphate hemihydrate, while the second one at ~165°C corresponding to the complete dehydration of the gypsum. Small exothermic effect appears around 350°C and is assigned to the phase transition of hexagonal anhydrite III to orthorhombic anhydrite II [10]. Total mass loses are similar for samples G1 and G2, while for G3 larger total mass loss was defined.

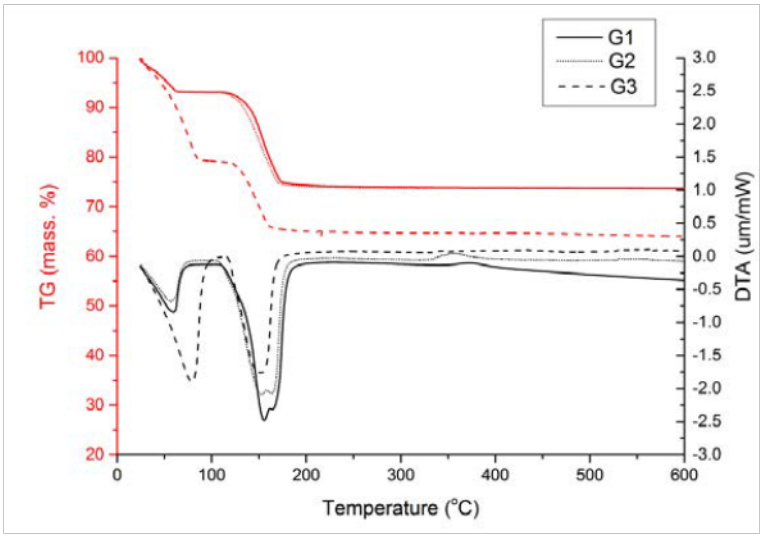

Figure 1: Thermal curves of the synthetic gypsum powders

3.2 XRD analysis

Qualitative analysis of the gypsums treated at different temperatures is shown in Fig 2. The results show, that in the temperature range of 80-90 °C, the gypsum starts to convert to basanite. The newly formed basanite is present in the samples up to 400 °C while with further increase in temperature it is fully converted to anhydrite.

Quantitative XRD was further performed on the samples treated at 40 °C, 200 °C and 300 °C in order to define the ratios of the different phases present in each sample. The results are shown in Table 1. The samples G1 and G2 exposed to temperature 40 °C are composed of gypsum (> 99 wt.) while only a very small fraction (< 1 wt. %) appears to be present as constituent phases in traces (quartz, calcite). The sample G3 composes fully of gypsum. After calcination at 200 °C, gypsum dehydrates completely to calcium sulphate hemihydrate (basanite) in all the investigated samples. The 1 wt. % of anhydrite defined in G3 at 200 °C was assigned to the effect of sample preparation. After the calcination at the temperature of 300 °C the basanite starts to convert to anhydrite. At this temperature of pre-treatment, the differences in the phase composition of the investigated gypsums are the most prominent. The highest quantity of basanite converted to anhydrite was characterized for the G2, while the smallest for the G3.

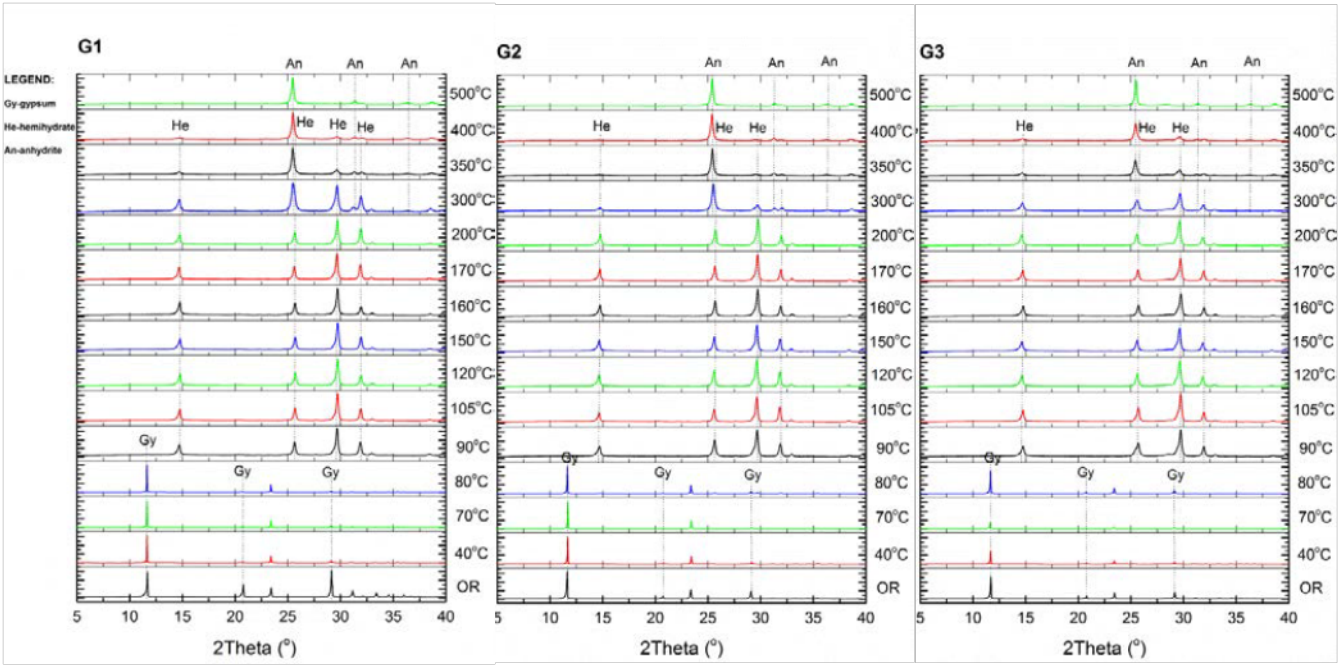

Figure 2: XRD patterns of the synthetic gypsum powders, pre-treated at different temperatures (OR: non-treated powder)

Table 1: QXRD analysis (wt. %) of phases within synthetic gypsum powders

Sample designation with temperature range (°C)	40°C			200°C			300°C		
	G1	G2	G3	G1	G2	G3	G1	G2	G3
Gypsum (wt. %)	99.3	99	100	0	0	0	0	0	0
Bassanite (wt. %)	0	0	0	100	100	99	71.8	36.3	93.8
Anhydrite (wt. %)	0	0	0	0	0	1	28.2	63.7	6.2

3.3 Scanning electron microscopy

Fig. 3 shows the effects of temperature treatment on gypsum powders microstructure. SEM images of powders exposed to the lower temperature present their different morphological appearance. Typical prismatic and short thick prismatic gypsum crystals were identified in powder G1. In G2, elongated gypsum crystals are prevailing over thick short prismatic crystals. The grains of G3 appear mostly in lenticular prismatic form. Twinned gypsum crystals are well defined in all the three of the samples. Calcination of the gypsum samples resembles in the surface morphology of the grains. As temperature increases, the etch pits are increasing on the grain surfaces and the stratification along the cleavage by the crystalline domains is expressed more distinctly.

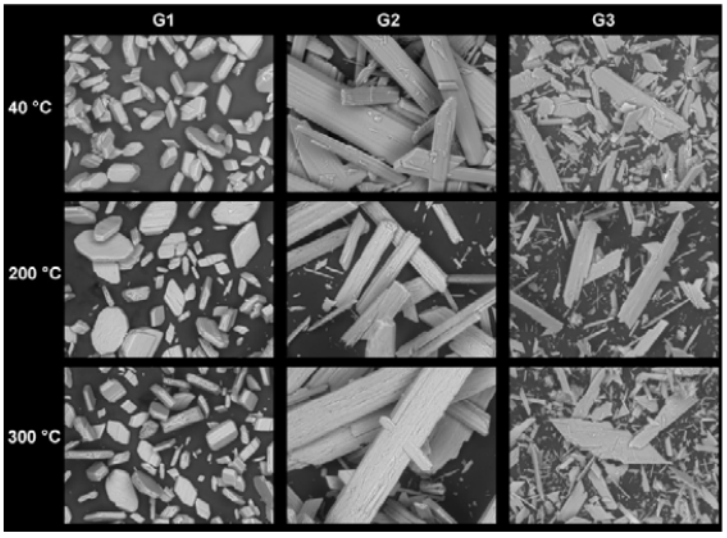

Figure 3: SEM microimages of the synthetic gypsum powders, pre-treated at different temperatures (400x magnification)

3.4 Setting time

The results of setting times are given in Table 2 and as is seen, setting times of all powders are very short, especially those which were exposed at higher temperatures. Setting times differs slightly between powders regarding the powder origin and different amount of present mineral phases. The results of gypsum powders, treated at 40 °C, have shown very prolonged setting time, even up to one day. The initial setting time decreases with the increasing temperature and decreased amount of bassanite, even less than 1 min. The final setting time ranges from 5 minutes to 13 minutes, regarding the chosen powder. The results were compared with the behaviour of reference powder, showing longer setting time. Our results are in comparison with the literature [20], where commercially obtained calcined gypsum initial setting time was 8 min and final 11 min (w/b=0.67 and 75 wt. % of bassanite). Rossetto et al. [18] have shown similar setting time of recycled gypsum plaster where initial setting time was 5.3 min and final 8.3 min (w/b=0.7 and 150°C for 4h).

The results have shown that with decreasing amount of basanite the setting time in powders is faster. Also small volume changes have occurred during setting. This needs to be highlighted, because volume instability may greatly affect the the properties of material in solid state [20]. After mixing gypsum powders with water, calcium sulphate hemihydrate starts to shrink immediately after it gets in contact with water. Further, it expands only slightly. The shrinkage is caused by the chemical reaction between the water and hemihydrate [20] while the expansion of gypsum during its setting is caused by the crystallization [20].

Table 2: Setting time (min) of synthetic gypsum powders

Sample designation with temperature range (°C)	Reference Zp151	200°C			250°C			300°C			400°C		
		G1	G2	G3	G1	G2	G3	G1	G2	G3	G1	G2	G3
Initial setting time (min, s)	17	7	6	<1	3,20	9	8	1,30	4	9,30	<1	<1	4
Final setting time (min, s)	27	9,20	8,30	-	5	11	13	2,30	6,30	13	-	-	8

4 CONCLUSIONS

Within this research, thermal analysis, mineralogical compositions and microstructure of thermally treated gypsums from different origin were analysed. Additionally the influence of calcination temperature on setting time was determined. On the basis of the research, it was found that the increase in temperature changed physical-chemical properties of powders and showed higher hemihydrate content. XRD results proved that calcination affected the hemihydrate formation, showing that the calcination condition was important for setting time. A temperature of 200 °C were found as adequate parameter to obtain considerable hemihydrate content and still performed setting time of 6-7 min. Therefore, such synthetic gypsum powders are very promising substitutes for commercial gypsum in additive technology, and consequently, it may lead to the mitigation of the environmental impact related to the waste gypsum production. Future studies must include additional research in the field of defining the influence of calcination temperature below 200°C and possible additives on setting time, as well as mechanical properties.

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