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Characterization of an anti-foaming and fast-setting gypsum for dental stone

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ABSTRACT

Objective. An anti-foaming and fast-setting gypsum for dental stone recently became available on the market. Interestingly, this product can be mixed by the cocktail shaking method, providing a more convenient way to obtain high reproducibility when fabricating error-free study models for digital dentistry. The aim of this study is to investigate setting time, surface bubble formation, and other gypsum characteristics of three dental stone products with different mixing methods.

Methods. Shake mix stone (SM), new plastone 2 white (NP), and Hi-Koseton (HK) were chosen. Using different mixing methods (cocktail shaking, hand mixing, hand mixing + vibrating, and hand mixing + vacuum process), the characteristics of dental stone were investigated according to ISO 6873. Powder size, morphology, and thermo/chemical analyses were performed.

Results. Regardless of the method of mixing, SM exhibited the fastest setting time (3–4 min) and the smallest number (~10% versus HK) and area (~30% versus HK) of surface bubbles among the investigated products, while setting expansion, mechanical properties such as compressive/impact strength and microhardness and detail reproduction before and after digital scanning were similar. A smaller size (~1.5 μm) and unidentified additives were revealed as possible reasons for the above anti-foaming and fast-setting characteristics.

Significance. Anti-foaming and fast-setting characteristics of a developed gypsum for dental stone were confirmed even with shaking.

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1. Introduction

Gypsum products are widely used in dentistry for fabricating study models and as auxiliary materials for dental laboratory operations due to cost efficiency and easy handling [1–3]. Depending on the specific properties necessary for a particular use, gypsum-based products are subcategorized into different compositions/formulas, from impression plaster (type 1) to improved stone (type 4 or 5) [4]. Among these categories, gypsum for dental stone (mainly type 3) is routinely used for preparing study or master models and impression materials. When calcium sulfate hemihydrate gypsum powder ($CaSO_4 \cdot 1/2H_2O$) is mixed with water and the mixture is poured into an impression/designed mould, setting occurs, and a specific morphology is achieved.

The main drawbacks of utilizing gypsum for dental stone are the time required and the pores present on the surface (or immediately below the surface), which delay laboratory processing and lead to inaccurate anatomical replicates for future work [5,6]. To tackle the above issues, myriad approaches (the addition of potassium sulfate/powdered gypsum, the regulation of water temperature to decrease the setting time, and the use of a vibrator or vacuum machine to remove bubbles) have been developed and used in the clinic [1,2,7]. However, these approaches are still suboptimal due to changes in other gypsum characteristics (e.g., mechanical properties, setting expansion, and detail reproduction ability), as well as inconvenient processes or preparation of the ingredients/device.

Recently, a fast-setting and anti-foaming gypsum for dental stone has become available with the inclusion of optimized additives (i.e., potassium sulfate, polycarboxylate, or cyclic siloxane) or polymer coating technology (acrylic polymer coating) in gypsum powder, providing fast-setting ability with enhanced dispersion and destruction of bubbles during setting [8–10]. Additionally, this product can be mixed by the cocktail shaking method, providing a more convenient methodology for achieving high reproducibility for the fabrication of dental gypsum-based products by unskilled clinicians.

Fast-setting dental gypsum without bubble formation is important in the continuously developing area of digital dental technologies, including CAD/CAM, 3D printing, and digital scanning/impression systems, for the rapid recovery of the oral anatomy with customized/digitalized dental prosthodontics/restoratives [11–14]. Because development of direct digital oral scanning is still on-going for optimizing accuracy and time-cost issue, conventional impressions and digital scanning of model stone have been widely used in dental clinics [15]. Thus, investigation of new dental gypsum in comparison to other products is needed to prove its clinical effectiveness even with the cocktail shaking method.

Therefore, the aim of this study is to compare the characteristics of gypsum for dental stone, such as setting time, setting expansion, compressive strength, detail reproduction before and after digital scanning, and anti-foaming effects, among commercially available products, including a newly developed 'anti-foaming and fast-setting gypsum', depending on the method of mixing (i.e., cocktail shaking, hand mixing, hand mixing + vibrating, and hand mixing + vacuum process). To reveal the underlying mechanism of the observed 'anti-foaming and fast-setting behaviours', powder size distribution, thermogravimetric, and elemental analyses were performed. The null hypothesis of this study is that there are no differences in setting time or bubble formation on the surface (1) among different products mixed with the same method or (2) among different mixing methods for the same gypsum product.

2. Materials and methods

2.1. *Dental gypsum and mixing methods*

The dental gypsum products used in this study include a newly developed Shake! Mix stone (SM, GC, Tokyo, Japan) and two types of conventional type 3 improved stone (new plastone II white (NP) and Hi-Koseton (HK)). The details of composition and characteristics given by the manufacturers, including the water/powder ratio, are summarized in Table 1. The gypsum materials were evaluated with reference to the International Standards Organization specifications for dental gypsum products (ISO 6873). When mixing, distilled water (DW) was used, and the amount of DW was determined according to the water/powder ratio provided in the manufacturer's instructions. The temperature and humidity during the experiment were set at (23 ± 2) °C and (50 ± 10) %, respectively. The mixing methods for preparing the specimens are described below. The shaking method used a Shake! Mix stone shaker (a plastic bottle with cap, GC, Tokyo, Japan) to mix the gypsum powder and DW for 20 s by cocktail shaking. The hand mixing method was performed for 30 s using a rubber bowl and a spatula. The vibration method was performed to remove air bubbles by using a vibrator (VIBRATOR-OSA, Osung, Gimpo, Korea) for 10 s after hand mixing for 30 s. The vacuum mixing method used a vacuum mixer (Twister, Renfert GmbH, Hilzingen, Germany) in a 500 ml mixing bowl for 30 s after hand premixing for 5 s to spread powder in DW. 5 s of hand premixing before vacuum mixing was chosen based on preliminary study. Vibrator mixing was performed only for the surface roughness, surface pore and pore size tests.

2.2. *Setting time*

Four hundred grams of gypsum powder was mixed at the water/powder ratio indicated in the manufacturer's instructions according to ISO 6873. The mixed gypsum powder was used to fill a cylindrical mould with a height of 40 mm, a lower inner diameter of 60 mm and an upper inner diameter of 70 mm. Measurements were made at 15 s intervals starting 2 min before the setting time listed by the manufacturer using a needle penetrometer (SJ-209, Sunjin Precision Industry, Seoul, Korea) in accordance with ISO 6873. Measurement of setting time started from the time when the gypsum powder was added to the water and end of setting time was determined when the needle first failed to penetrate the specimen to a depth of 2 mm (n = 3). Loss of gloss time as an initial setting time was measured when the gloss disappeared from the gypsum surface (n = 3).

Table 1 – Product details for the dental gypsum products used in this study.

Material	Mixing method	Abbreviation	Composition	Water/powder (W/P)	Setting time (min)	Linear setting expansion after 2 hr (%)	Compressive strength after 1 hr (MPa)	Lot	Manufacturer	
Shake! Mix Stone (SM)	Shaking	SM-Sh	Plaster of Paris (100%)	25/100	2.2	0.13	40	1711152	GC	Japan
	Hand mixing	SM-Ha								
	Vibration	SM-Vi								
	Vacuum	SM-Va								
New plastone IIwhite (NP)	Shaking	NP-Sh	Zin White (1%), Anatase (5%), Plaster of Paris (89%), Silica (5%)	23/100	11	0.25	49	1704242	GC	Japan
	Hand mixing	NP-Ha								
	Vibration	NP-Vi								
	Vacuum	NP-Va								
Hi-Koseton (HK)	Shaking	HK-Sh	Gypsum hemihydrate (99%)	24/100	10	0.24	35	1101172	Maruishi	Japan
	Hand mixing	HK-Ha								
	Vibration	HK-Vi								
	Vacuum	HK-Va								

2.3. *Linear setting expansion*

An extensometer with a trough with a triangular cross-section was used, and all procedures followed ISO 6873. Briefly, a mould release agent (Vaseline, Unilever, Seoul, Korea) was applied to the surfaces at which the gypsum and the trough were in contact, and 200 g of gypsum was then mixed and used to fill the trough to generate a surface with a flat top. The initial length of the specimen was set at 0 using a 1 μm dial gauge (2109F, Mitutoyo, Tokyo, Japan). The linear setting expansion was measured after 1, 2, 4, 8 and 24 h (n = 3).

2.4. *Reproduction of detail and scannability*

A dental rubber elastomeric impression material (Exafine Injection Type, GC, Tokyo, Japan) was injected into a detail reproducibility block with 20, 50 and 75 μm detail lines according to ISO 6873, and the glass plate was covered and cured by applying a load of 1500 g. After separating the impression material from the detail reproducible block, a ring was made of dental wax (Crystal wax, Dae-Dong Inc., Daegu, Korea). After mixing 200 g of gypsum using a vibrator, the gypsum was poured. After 1 h, the gypsum was separated from the impression material. The separated gypsum was measured at the 20, 50, and 75 μm detail lines with a 5 × magnification using a super precision lighting magnifier (BD102-5X, Seiki, Seoul, Korea). Each sample was given a score from 1 to 3 (n = 5) according to the modified methodology in Ref. [16]. A score of 1 was given when no line was reproduced, a score of 2 was given when a line was reproduced but not continuous, a score of 3 was given when a line was reproduced continuously. After measurement, the detail lines were digitally scanned using a dental CAD/CAM scanner (D700, 3shape, Copenhagen, Denmark) to investigate scannability (n = 5).

2.5. *Mechanical properties*

Compressive strength was determined by modified ISO 6873 (n = 5) due to upper limitation of load cells. The original size (a diameter of 20 mm and a length of 40 mm) of mould decreased to a diameter of 15 mm and a length of 30 mm, maintaining ratio between diameter and length (1:2), as referenced elsewhere [5]. Briefly, the size of the specimens was produced with a silicone mould (ELITE DOUBLE 22, Zhermack, Ro, Italy) with a diameter of 15 mm and a height of 30 mm. Two hundred grams of gypsum was poured into the silicone mould after mixing using a vibrator. After passing through the loss of gloss stage, a 400 g glass plate and 1.1 kg of weight (total 1.5 kg) were pressed against the top surface of the mould to align the specimen. After 45 min of mixing, the mould was removed and stored at (23 ± 2) °C and (50 ± 10) % relative humidity until mechanical testing. The compressive strength was measured at a rate of 2.0 mm/min using a universal testing machine (10 kN load cells, Instron 5960, Instron, MA, USA) 1 h and 24 h after the start of mixing. The compressive strength was calculated by the following formula:

$S = F/\pi r^2$ (S is the compressive fracture stress (MPa), F is the recorded maximum force (N) and r is the measured radius of specimen (mm))

The impact strength was determined by the standard Dynstat impact bending test (DIN 53,435, n = 5). Dynstat impact test is usually used for components made of plastics or composite. From clinical point of view, resistance against outer force is important to maintain the outer morphology of dental stone, thus impact test was used to evaluate the mechanical strength [17]. Here, due to easiness of sample preparation and test methodology, Dynstat impact bending test was utilized for measuring mechanical strength as trial among other methodologies [18,19]. A mould with a length of 15 mm, a width of 10 mm, and a height of 4.5 mm was prepared to produce the impact strength specimen. Fifty grams of gypsum was mixed for each group, and five specimens without notches were prepared and poured into a mould using a vibrator. After 1 h and 24 h from the start of mixing, a pendulum impact testing machine (HIT5.5 P, Zwick, Ulm, Germany) was set with a 0.2J pendulum to perform the Dynstat impact bending test. The impact strength was calculated based on the methodology in the DIN 53435 standards.

Microhardness was determined using a specimen for the impact bending test (n = 5). Vicker hardness was measured using a hardness tester (HM-221, Mitutoyo, Tokyo, Japan) with a 2000 gf load for 10 s, and the average of triplicate measurements was used for the value of each specimen.

2.6. *Surface pores and total pore area*

For the preparation of specimens, a mould with a diameter of 40 mm and a height of 6 mm was fabricated with a dental rubber elastic impression material (Master Sil Light Body, SEIL GLOBAL, Busan, Korea). One hundred grams of gypsum were mixed by the indicated mixing method and poured into an impression material mould (n = 5). Five specimens per mixing method were photographed at a magnification of 100 × using a metal microscope (S39B, MIC, Winona, USA) and a digital microscope camera (Eyecam, MIC, Winona, MN, USA). The pores on the surface were measured at 5 sites per specimen and then summed. Centre field of specimen and other four field from different directions (North, South, West and East from centre field) 10 mm apart from centre were captured. The pore size (lower limit is 0.3 mm) was measured by an image measurement program (ImageJ 1.46 version, USA) and then summed.

2.7. *Surface roughness*

The surface roughness (arithmetic mean deviation of the profile (Ra)) was measured by a surface roughness metre (SJ-400, Mitutoyo, Kawasaki, Japan, n = 5) using same specimen for pore measurement. Measuring length, cut-off values, and scan speed is 4 mm, 0.8 mm and 0.5 mm/s respectively. The average value of three measurements was determined as the value for each specimen.

2.8. *Grain size and morphology*

To measure the particle size of the gypsum powder, 20 mg of each material was placed in DW using an electronic balance (Explorer EX224G, OHAUS, NJ, USA) and evenly dispersed in an ultrasonic machine (Power Sonic 410, Hwashin Technology, Seoul, Korea) for 30 min [20]. Two measurements were made for each material using a particle size analyser (LA-950V2, HORIBA, Kyoto, Japan). Furthermore, each material was visualized at a 2000 × magnification using an Fe-SEM (Sigma, ZEISS, Oberkochen, Germany).

2.9. *Thermogravimetric analysis (TGA)*

A thermogravimetric analyser (Thermo Plus Evo II, Rigaku, Tokyo, Japan) was used to measure the change in weight over temperature. 9 ± 0.5 g of gypsum powder was used to measure and standard materials (Al_2O_3) was used as counterpart. TGA was performed by heating from room temperature to 1000 °C at an ascending rate of 5 °C per minute in a nitrogen atmosphere.

2.10. *X-ray photoelectron spectroscopy (XPS)*

XPS (K-alpha, Thermo Scientific, UK) was used to analyse the elements in the dental gypsum using monochromated Al K-alpha (1486.6 eV) at 12 kV and 3 mA under a pressure of 4.8×10^{-9} mb. The resolution of the detailed scan was measured as 0.7 eV using Ag 3d5/2 peaks. The survey and detailed scan step sizes were determined at 1 and 0.1 eV, respectively. C1s at 284.8 eV was used as a reference. C, Ca, O, P, S, Si, K, and Zn were detected in detail. Representative data are shown after triplicate surface analysis.

2.11. *Statistics*

Statistical analysis was performed with a one-way analysis of variance (ANOVA) with the Tukey honest significant differences test as a post hoc test (IBM SPSS Statistics v23.0; IBM Corp) ($P = 0.05$). Normal distribution test was performed by Shapiro–Wilk test. For analysing statistics of detail reproduction score, Kruskal–0Wallis test was performed with the Dunn procedure as a post hoc test ($P = 0.05$)

3. Results

3.1. *Setting time and setting expansion*

Initially, to investigate the setting time of a newly developed dental gypsum (SM) and two other dental gypsum products (NP and HK) with different kinds of mixing methods, three different mixing methods (Fig. 1a), shaking, hand mixing only, and vacuum mixing, were performed to mix the dental gypsum powder and DW. When mixing with DW according to the manufacturer's protocol, SM (3–4 min) had a much shorter (approximately three times shorter) setting time than the other products (NP and HK, 10–13 min). In contrast to SM, NP and HK showed a significant increase in the total setting time with the shaking method compared to the use of a vacuum machine ($P < 0.05$, Fig. 1b).

3.2. *Physicomechanical properties*

Physicomechanical properties such as linear expansion and physical properties such as compressive strength, impact strength, and Vickers hardness were investigated. The three different mixing methods did not affect the linear expansion of SM and HK until 24 h, while NP showed a significant decrease in linear expansion at 24 h with the shaking method compared to the hand mixing and vacuum methods (Fig. 2a). The manufacturer's linear expansion of SM at 2 h after the start of mixing (0.13%) was within the range of the values obtained in this experiment, while that of NP and HK (0.25 and 0.24%) was slightly over the range of the values obtained in this experiment (Table 1).

The mean compressive strengths and their standard deviations in MPa are presented in Fig. 2b. The 1 and 24 h compressive strength values of the different dental gypsum groups did not show any significant differences among mixing methods under all conditions ($P > 0.05$), except for HK at 24 h, which showed a difference between shaking and hand or vacuum mixing($P < 0.05$). In the case of impact strength, only HK at 1 h showed a significant difference between shaking and hand or vacuum mixing ($P < 0.05$), while SM and NP were not influenced by the method of mixing ($P > 0.05$). Vickers hardness seemed to be increased with vacuum mixing compared to the other methods for almost all dental gypsum products at 1 and 24 h.

3.3. *Detail reproduction and scannability*

Detail reproduction ability and scannability were investigated. Before scanning, as-given set stone from all dental gypsum products showed detail reproduction scores of 2.8–3 at 20 μm, with perfect detail reproduction at 50 and 75 μm (Fig. 3a). For all groups, there was no significant difference in detail reproduction among the mixing methods before and after scanning ($P > 0.05$). But, after scanning, the detail reproduction score at 20 μm from digital images scanned by machine was decreased down to 1 from the score before scanning (2.8–3) in all conditions (Fig. 3a), while detail reproduction at 50 and 75 μm was maintained, as confirmed by optical/scanned images of the dental gypsum before and after scanning (Fig. 3b and sFig. 1).

3.4. *Surface porosity and area*

The mean surface porosity showed significant differences when the different dental gypsum products and mixing methods were compared (Fig. 4a). SM showed a relatively small number of pores (4–9 pores per 5 random fields) on the surface compared to NP and HK (5–15 pores for NP and 20–55 pores for HK) in all mixing conditions, as confirmed by the quantification of total pore numbers by ImageJ. In particular, shaking and vacuum mixing showed similar low pore numbers ($\tilde{5}$) with SM, while NP and HK exhibited a much higher number of pores with the shaking method than with vacuum mixing. When total pore area and surface roughness were compared among products and mixing methods, a roughly similar trend appeared for SM; SM and NP showed a relatively small total pore area (0.15–0.25 mm^2 from 5 random images) on the surface compared to HK (0.4–0.5 mm^2 from HK) in all mixing conditions. In addition, shaking and vacuum mixing showed a similar lower total pore area for SM and NP, while HK exhibited a much higher total pore area with the shaking method than with vacuum

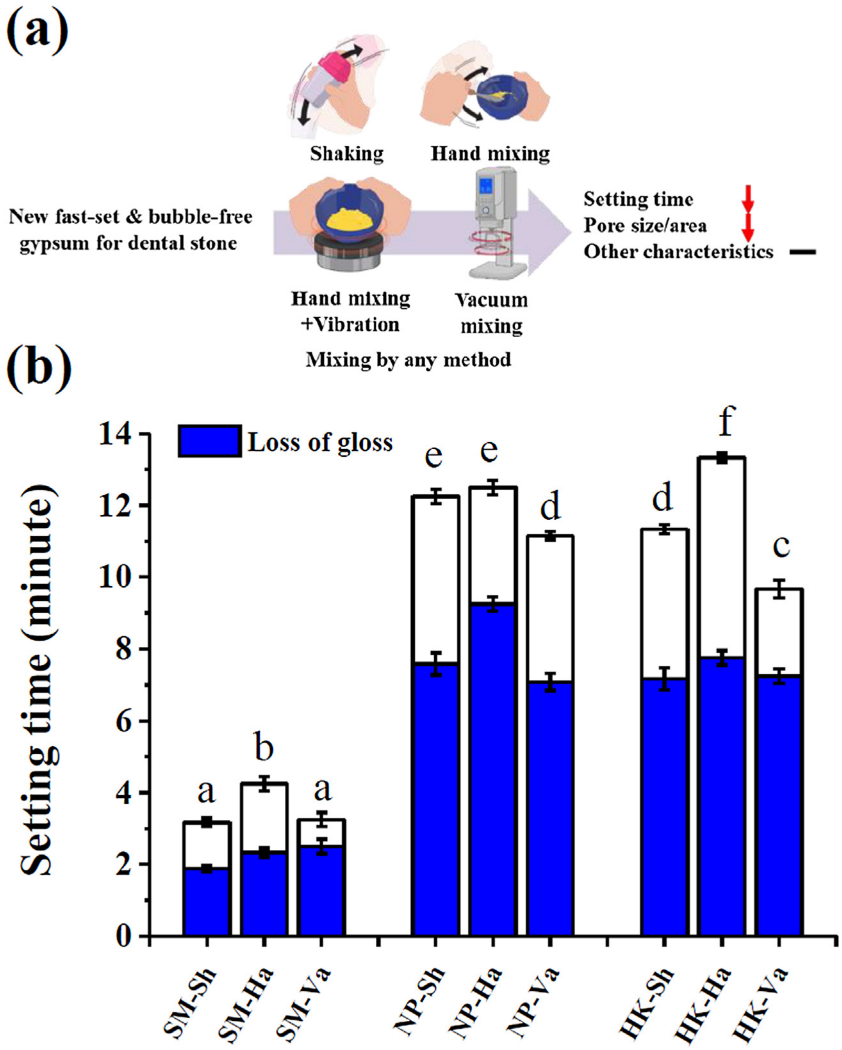

Fig. 1 – Schematic diagram of this investigation using different mixing methods (a) and setting times for dental gypsum (b). Fast setting time (loss of gloss) was observed with SM regardless of the mixing methodology (even by the cocktail shaking method). Different letters indicate significant differences among samples (n = 3, $P < 0.05$).

mixing. Surface roughness was maintained for SM and NP regardless of the mixing method, while shaking generated a much higher surface roughness than vacuum mixing for HK.

3.5. *Study of the mechanism of the fast-setting and anti-foaming characteristics*

Powder size, morphology and components were investigated to study the mechanism of the observed fast-setting and anti-foaming effects. Initially, the size distribution was evaluated, and a relatively low powder size with an even size distribution was detected for NP compared to SM and HK, with mean sizes and standard deviations of 0̃.6 (±0.7), 1̃.5 (±0.9), and 3̃.0 (±1.4) µm, respectively (Fig. 5a). The powder size of each group, as visualized by SEM, was consistent with the powder size distribution results, with NP < SM < HK in ascending order (Fig. 5b). The morphology of the powder was irregular, not globular or evenly shaped. To investigate polymer inclusion in the powder that might decrease the setting time or provide anti-foaming ability, such as polyethylene glycol or polycarboxylate, a thermogravimetric analyser was used to measure the change in weight over temperature from room temperature to 800 °C. All groups showed a 6–7% reduction of weight until 200 °C, mainly due to dehydration (removal of $1/2(H_2O)$) of hemihydrate calcium sulfate (hemihydrate gypsum, $CaSO_4 \bullet 1/2(H_2O)$), resulting in the formation of calcium sulfate ($CaSO_4$, 136.14) after reduction of the theoretically calculated hemihydrate weight (6.2%, 9.0/145.15, Fig. 5c). Furthermore, XPS analysis was performed to investigate the inclusion of additional elements in the gypsum powder (Fig. 5d and Table 2). All products showed Ca, S, O, C, and P as the major elements in hemihydrate gypsum (Ca, S, O, and C) and its impurities (P from phosphogypsum). In contrast to HK, SM and NP contained Zn as a reinforcement (Zn from ZnO) to resist outside force. Interestingly, SM alone showed a potassium peak, which is a possible indicator of potassium sulfate as a fast-setting component (Fig. 5e). The Si peak was detected in NP (manufacturer's composition) and SM (not mentioned in detail) but not HK. The

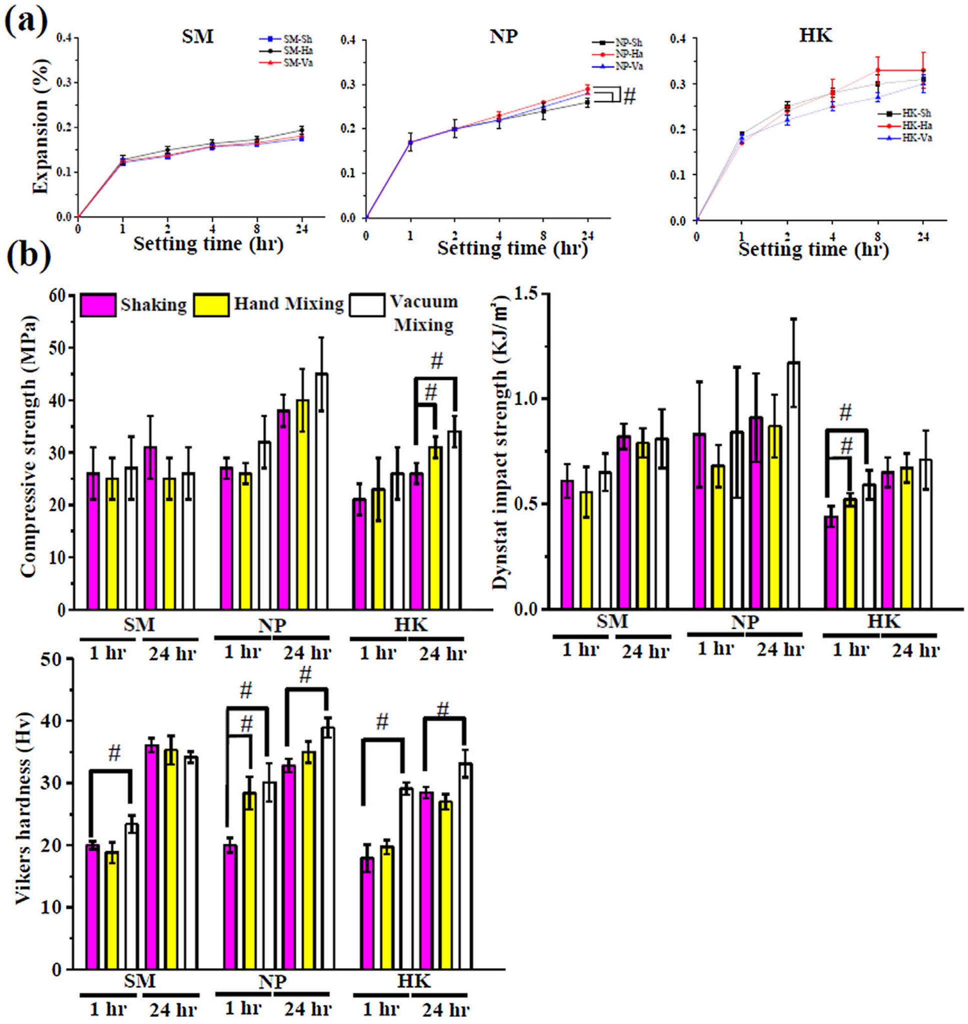

Fig. 2 – Linear expansion of dental gypsum up to 24 h (a) and mechanical properties (b) including compressive strength, impact strength and microhardness. Regardless of the mixing method, SM revealed similar linear expansion and mechanical properties (even with the cocktail shaking method). # indicates significant differences (n = 3 for linear expansion and n = 5 for mechanical properties, $P < 0.05$).

Table 2 – XPS analysis results of dental gypsum (average ± standard deviation).

Atom/product	SM			NP			HK		
	At.%	/Ca	/S	At.%	/Ca	/S	At.%	/Ca	/S
C1s	12.57 ± 0.27	0.83 ± 0.01	0.73 ± 0.03	23.96 ± 0.50	1.75 ± 0.08	1.52 ± 0.01	25.88 ± 0.31	1.94 ± 0.07	1.70 ± 0.02
Ca2p	15.06 ± 0.56	1.00 ± 0.00	0.88 ± 0.04	13.7 ± 0.35	1.00 ± 0.00	0.87 ± 0.05	13.33 ± 0.30	1.00 ± 0.00	0.88 ± 0.04
O1s	52.70 ± 0.56	3.50 ± 0.16	3.07 ± 0.03	45.71 ± 0.45	3.34 ± 0.05	2.90 ± 0.11	44.16 ± 0.15	3.31 ± 0.06	2.91 ± 0.09
P2p	0.16 ± 0.04	0.01 ± 0.00	0.01 ± 0.00	0.16 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	0.32 ± 0.04	0.02 ± 0.00	0.02 ± 0.00
S2p	17.17 ± 0.24	1.14 ± 0.05	1.00 ± 0.00	15.77 ± 0.41	1.15 ± 0.06	1.00 ± 0.00	15.2 ± 0.40	1.14 ± 0.06	1.00 ± 0.00
Si2p	1.27 ± 0.04	0.08 ± 0.00	0.07 ± 0.00	0.42 ± 0.04	0.03 ± 0.00	0.03 ± 0.00	1.10 ± 0.10	0.08 ± 0.01	0.07 ± 0.01
K2p	0.63 ± 0.03	0.04 ± 0.00	0.04 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Zn2p3	0.45 ± 0.05	0.03 ± 0.00	0.03 ± 0.00	0.28 ± 0.02	0.02 ± 0.00	0.02 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

normalized ratios of Si and K to the major element in dental gypsum (Ca or S) were higher for SM than for NP or HK.

4. Discussion

The null hypothesis in this study (that there is no difference in setting time or bubble formation on the surface (1) among different products with the same mixing method and (2) among different mixing methods with the same gypsum product) was rejected. The present investigation was designed to evaluate a newly introduced dental gypsum, which reduces setting time and bubble formation even with cocktail shaking. This product was compared to other conventionally used dental gypsums, NP (from the same company) and HK (a well-known market

(a)

	As-given set stone			Digital image after scanning		
µm	20	50	75	20	50	75
SM-Sh	2.8±0.4	3±0	3±0	1.2±0.4*	3±0	3±0
SM-Ha	2.6±0.5	3±0	3±0	1±0*	3±0	3±0
SM-Va	2.6±0.5	3±0	3±0	1.4±0.5*	3±0	3±0
NP-Sh	2.8±0.4	3±0	3±0	1.4±0.5*	3±0	3±0
NP-Ha	2.8±0.4	3±0	3±0	1.2±0.4*	3±0	3±0
NP-Va	3±0	3±0	3±0	1.4±0.5*	3±0	3±0
HK-Sh	2.4±0.5	3±0	3±0	1±0*	3±0	3±0
HK-Ha	2.6±0.5	3±0	3±0	1.2±0.4*	3±0	3±0
HK-Va	2.8±0.4	3±0	3±0	1.2±0.4*	3±0	3±0

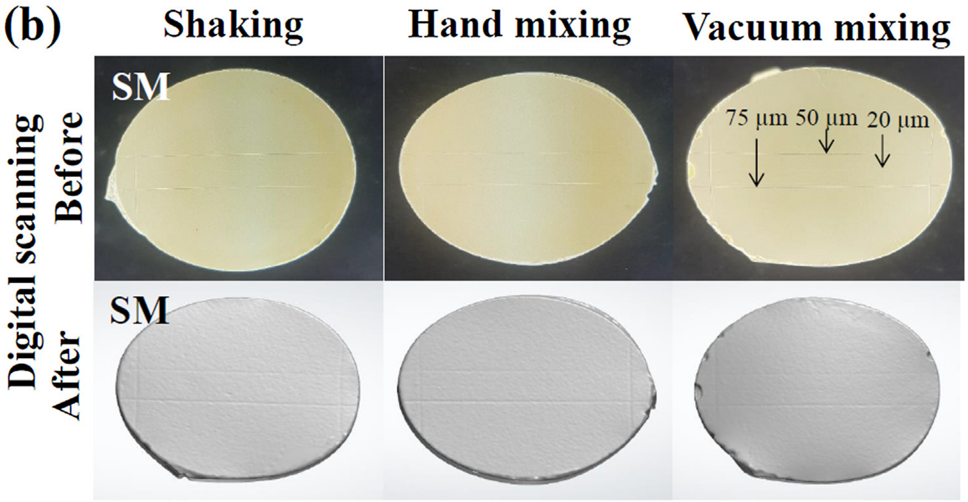

Fig. 3 – Detail reproduction score (average and standard deviation, n = 5) before and after digital scanning (a) and representative images of SM (b). Representative optical data before and after scanning for NP and HK appear in the Supplementary Data (sFig. 1). Regardless of the mixing methodology, comparable detail reproduction of 20, 50 and 75 µm was observed for SM before and after digital scanning, ($P > 0.05$) while decrease of detail reproduction was observed at 20 µm after scanning (*, $P < 0.05$).

product), in terms of some of the physicomechanical properties of the resultant stone. It is worth noting that the stone materials used in this study meet the required values set forth by ISO 6873 for gypsum products.

When the patient oral anatomy is recorded by an impression material (mostly alginate or elastomeric impression materials) to make a study or final model, dental stone (including types 3 and 4) is poured into the impression material, set, and 3D scanned to transform the anatomical morphology into digital data for further digital/laboratory processing. Thus, fast-setting and anti-foaming ability (which reduces bubbles in the set study model) are needed, along with developed digital dental technology and ongoing digital dentistry.

Here, the fast-setting property of newly developed dental gypsum (3–4 min) was confirmed after comparison to setting time results from other conventional dental stone materials (10–13 min), which can be achieved by any mixing methodology: cocktail shaking, hand mixing, and vacuum mixing. To investigate the setting time of a newly developed dental gypsum (SM) with different kinds of mixing methods, three different mixing methods (Fig. 1a), shaking, hand mixing only, and vacuum mixing, were performed to mix the dental gypsum powder and DW. As controls, two other conventionally used dental gypsum products (NP (from the same company) and HK (a well-known market product)) were chosen. The setting time of all materials measured in this study was within 20% of the value included in the manufacturer's information, a requirement of the ISO standard (2.33 (180 s, SM), 11 (NP), and 10 (HK) min). Previous investigations suggested that vacuum mixing provides a fast setting time and less bubble inclusion on the surface than hand mixing [5], which is why vacuum mixing has been used in dental clinics and dental laboratories as a gold standard mixing methodology [2]. The shaking method has not been considered as a conventional mixing technology because of the potential for many entrapped bubbles inside of the stone and non-homogenous mixing [5]. However, SM showed a similar 3–4 min setting time regardless of the mixing methodology, while other materials exhibited a faster setting time with vacuum mixing, which was consistent with previous studies [5,21,22].

To analyse whether the fast setting time of SM, even with shaking mixing, adversely affects other physicomechanical properties essential for dental gypsum products (mostly suggested by the ISO standard for dental gypsum), linear expansion and various physical properties (compressive strength, impact strength, and Vickers hardness) were investigated. Regardless of the mixing method, SM showed similar linear expansion as a basic conventional physical

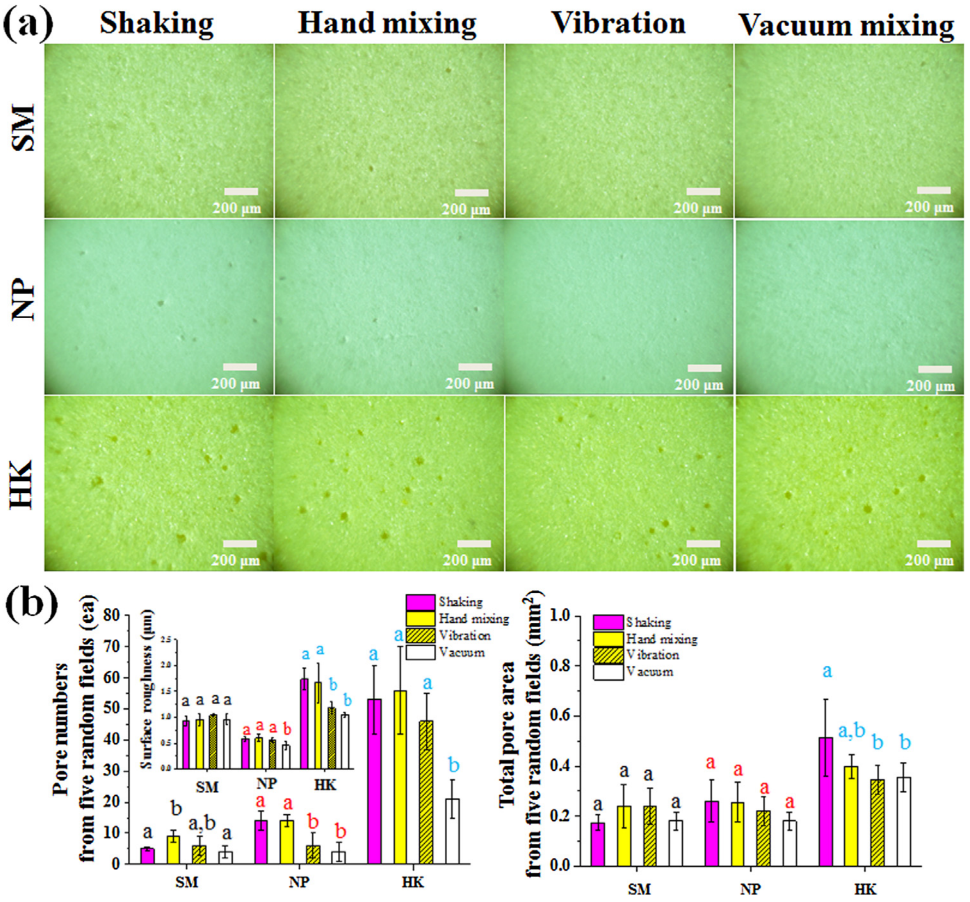

Fig. 4 – Optical images of bubbles on the set dental gypsum (a). Quantification of the average number of bubbles and total area from five random fields in each specimen (b). Fewer bubbles and areas were observed for SM than for the other materials, even with shaking. Insert graph representing surface roughness. Different letters in the same colour indicate significant differences among samples (n = 5, P < 0.05).

property, indicating no adverse effect of the shaking methodology on linear expansion. Most other mechanical properties, including compressive strength (suggested by the ISO standard for dental gypsum) using a modified specimen size from the ISO standard (after consideration of the limitation of the universal testing machine used in this experiment), impact strength (resistance to damage after falling), Vickers hardness (resistance to an outside mechanical force during handling) were maintained in SM regardless of the mixing methodology, while the other materials (NP and HK) exhibited an increase in mechanical properties after vacuum mixing compared to shaking and hand mixing, which was consistent with the previous literature [5,23]. Although different specimen sizes were used to test compressive strength, the values obtained here met the requirement of the ISO standard (minimum of 20 MPa 1 h after the start of mixing) [4].

Detail reproduction and digital scannability by a digital scanner are essential for the use of dental gypsum in replicating anatomical structure with accuracy. A fast setting time might affect negatively detail reproduction and scannability by a 3D scanning machine for CAD/CAM laboratory works. Thus, detail reproduction ability and scannability were investigated. Regardless of the mixing method, detail reproduction ability was maintained in all set products, meeting the requirement of the ISO standard (complete reproduction of 50 and 75 µm width lines (scores of 3 at both 50 and 75 µm)). The 20 µm width line was partially reproduced (not continuous (score 2) in some specimens, giving a score of 2.4–3.0 on average for all products with different mixing methodologies. After scanning, detail reproduction of the 50 and 75 µm width lines was achieved regardless of the product or the mixing method, but the 20 µm line was rarely reproduced (score 1–1.4).

Lastly, bubble formation on the surface was analysed to determine whether SM had anti-foaming ability even with the shaking method. Compared to the other materials, SM showed less air bubble inclusion, as determined by pore numbers and area, after both shaking and vacuum mixing, which was supported by the results from surface roughness measurements. Interestingly, SM showed similar low bubble inclusion for both shaking and vacuum mixing, while HK showed higher bubble numbers and total bubble area after shaking than after vacuum mixing, which was consistent with previous results. After considering the special indication of NP as a type 3 dental gypsum, which was developed for fabricating an orthodontic study model with a smooth and

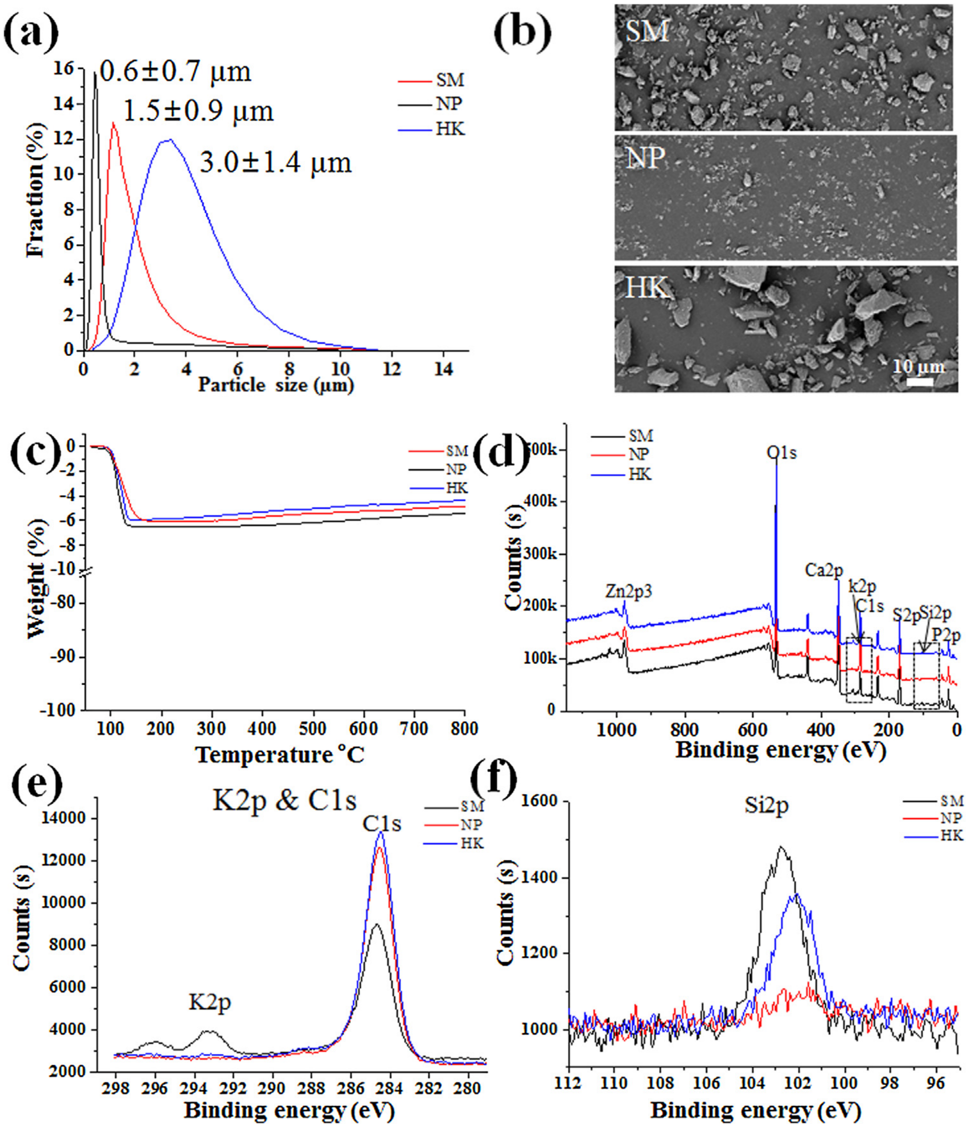

Fig. 5 – Study of fast-setting and anti-foaming mechanisms. Particle size analysis results (a) and morphology by SEM (b). Thermogravimetric analysis to detect polymeric additives (c) and XPS analysis to investigate elements in the additives (d–f) were performed. Only a theoretical reduction of weight (6–7%) due to dehydration of hemihydrate calcium sulfate, resulting in a 6.2% reduction of weight (calculated based on the elements in hemihydrate and hemihydrate calcium sulfate, see manuscript for detailed calculation), was observed in all groups, revealing the possible addition of polymeric molecules within the limits of thermogravimetric analysis. However, the XPS peaks of K2p and Si2p revealed the possible inclusion of potassium sulfate (for fast-setting) and cyclic siloxane (for anti-forming) as additives in the dental gypsum.

highly polished surface, less bubble formation and a great anti-foaming ability, and comparable properties mentioned above from SM, SM seemed to be applicable for a conventional type 3 dental gypsum with strong advantage of less air bubble formation compared to NP, will be confirmed by further investigation.

Many factors, including powder characteristics (size, shape, distribution, and morphology) and additives in the dental gypsum, affect setting time and anti-foaming ability; small size, even distribution, and spherical morphology promote fast-setting and anti-foaming ability in dental gypsum [1,2]. Here, without a special morphology of the powder, an evenly distributed particle size with a small diameter (0̃.6 ± 0.7) was observed for NP rather than SM (1̃.5 ± 0.9) and HK (3̃.0 ± 1.4), showing a relatively large distribution with a larger powder size, implicating a partial role of particle characteristics. To reveal the major reasons for fast-setting and anti-foaming ability, TGA for detecting any polymeric additives and XPS analysis for investigating the elements in the additives were performed. Only a theoretical reduction of weight (6–7%) due to dehydration of hemihydrate calcium sulfate, resulting in a 6.2% reduction of weight (calculated based on the following formula: $9.0(1/2(H_2O) / 145.15(CaSO_4 \bullet 1/2(H_2O))$, was observed in all groups, implying that no distinct polymer inclusion was observed in SM at the limited resolution of TGA (0̃.1%). However, XPS analysis revealed two important distinguishable peaks (K and Si) with relatively high proportions (0.63% of K and 1.27% of Si), indicating the possible existence of additives in SM. According to the patents issued by the manufacturer of SM [8,9], the fast-setting dental gypsum was generated by the addition of polycarboxylates (0.05–0.8 wt%) and potassium sulfate (K_2SO_4, 0.5–3 wt%), and anti-foaming was generated by the inclusion of an acrylic polymer (0.5–4 wt%) as a coating polymer to yield a repulsion among gypsum powder or cyclic siloxane ($SiO(CH_3)_2$, 0.001Õ.2 wt%) as an anti-foaming agent. Polycarboxylates and potassium sulfate are well-known additives for enhancing flowability and fast-setting of gypsum [10,24]. Polycarboxylates can have a surface activation function as water-reducing agents, decreasing the viscosity of the slurry without changing the powder-to-water ratio and, in turn, increasing workability, which might be beneficial for rapid dispersion of the stone powder in water and high detail reproduction ability of dental stone. However, the use of ordinary water-reducing agents, such as lignin sulfonate, a naphthalenesulfonate salt, an oxycarboxylate salt, a melaminesulfonate salt, a polystyrene sulfonate salt and a polycarboxylate salt, in dental gypsum powder considerably delays the setting time; thus, the water-reducing agent has not been used alone for dental stone, which requires a short setting time [8]. Therefore, fast-setting additives, such as potassium sulfate, sodium hypochlorite, slurry water, and terra alba (0.5–1 wt%), which accelerate the crystallization of dihydrate calcium sulfate, have been used to conjugate with the water-reducing agent to obtain optimal workability with a fast setting time [7]. According to the published literature and patents issued with respect to fast-setting, the XPS analysis performed in the current study, and other characteristics of the dental stone, SM seems to contain potassium sulfate as a fast-setting additive. However, the inclusion of polycarboxylate was not proven due to the detection limits of TGA and FT-IR (not shown). As possible new technologies applied in SM to decrease bubble formation, the inclusion of cyclic siloxane ($SiO(CH_3)_2$) and an acrylic polymer coating in SM gypsum powder was possibly suggested and XPS analysis, revealing distinct Si peaks compared to the other materials (especially versus NP), slightly supported above possibility. Although cyclic siloxane is known to be used in cosmetic and biomedical applications as an anti-foaming reagent by reducing the surface tension of air bubbles and ultimately destroying them, further investigation is needed to reveal the exact mechanism of the anti-foaming ability derived from the inclusion of cyclic siloxane in dental gypsum [8,25,26]. Like the inclusion of polycarboxylate, the addition of acrylic polymer coating technology to the gypsum powder for water reduction (increased fluidity or workability) was only assumed based on the manufacturer's patents, which is a limitation of this investigation [8].

5. Conclusion

This investigation evaluated the fast-setting and anti-foaming effect of a newly developed type 3 dental stone (SM), even when mixed by the cocktail shaking method. SM was compared to other conventionally used dental gypsums, NP (from the same company) and HK (another market product), in terms of some of the physicomechanical properties of the resultant stone. Within the limitations of this study, the following conclusions were drawn. (1) SM had an approximately 3 times faster setting time than the other dental gypsum products, with great anti-bubble ability and additions such as potassium sulfate for fast-setting and cyclic siloxane for anti-foaming. (2) Shaking proved to be an acceptable alternative to traditional mixing methods for SM, without affecting the physicomechanical properties of the set stone. (3) SM mixed by shaking can be properly digitally scanned, similar to other mixing methods (i.e., by hand, with a vibrator or with a vacuum machine).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.dental.2019.08.110.

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