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Evaluation of Some Physical Properties of Die Stone Made From Local Raw Gypsum Material

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الخلاصة

الأهداف: تهدف الدراسة الى تحضير أحد المنتجات الجبسية والتي لم يتم تحضيرها مسبقا في العراق وتتمثل بالنوع الرابع من مادة الحجر السني ، وذلك بواسطة تجفيف الجبس الطبيعي من خلال عملية غلي مع محلول كلوريد الكالسيوم بتركيز 30%. ومن ثم تقييم بعض الخصائص الفيزيائية للنوع الرابع من مادة الحجر السني المحضّر ليتيح استخدامه في مجال طب الأسنان.المواد وطرائق البحث: التقييم شمل نسبة الماء إلى المسحوق، زمن التجمد، و المقاومة الانضغاطية. إن النوع الرابع من مادة الحجر السني المحضّر محلياً المستخدم في هذه الدراسة كمجموعة تجريبية والانواع الثلاث الاخرى من المنتجات الجبسية التجارية والتي هي النوع الرابع من مادة الحجر السني التجاري، النوع الثالث من مادة الحجر السني (Elite) والجبس العراقي، كلها تمثل المجموعة القياسية إن نتائج القياسات أعلاه قد أُخضعت لتحليلات وصفية (الانحراف المتوسط والقياسي)، التحليلات أحادية الاتجاه للتفاوت (ANOVA) لتوضيح فيما إذا كان هناك أي اختلاف هام بين المجموعات التجريبية واختبار المقارنة المتعددة لـــ (Dunnett Pairwise) لعرض مستوى الأهمية المتمثل في كل مجموعة .النتائج: أظهرت نتائج هذه الدراسة بان ليس هناك اختلافات معنوية بين النوع الرابع من مادة الحجر السني المحضّر محلياً والآخر التجاري من ناحية نسبة الماء إلى المسحوق و زمن التصلب (عند مستوى اختلاف معنوي $P\leq 0.05$) . لكن هناك اختلاف معنوي في المقاومة الانضغاطية ؛ وكذلك يوجد اختلافات معنوية في كل الخصائص الفيزيائية المذكورة أعلاه بين النوع الرابع من مادة الحجر السني المحضّر محلياً، النوع الثالث من الحجري السني (Elite) والجبس العراقي. الاستنتاجات: إن النتائج توضح بأن الخصائص الفيزيائية بين النوع الرابع من مادة الحجر السني المحضّر محلياً يقارب الخصائص الفيزيائية للمنتج التجاري وذلك طبقاً تعليمات منظمة طب الأسنان الأمريكية (ADA) فيما يتعلق بالمنتجات الجبسية.

ABSTRACT

Aim: The aim of this study was to prepare die stone material by dehydration of the local natural raw gypsum in boiling with 30% calcium chloride solution , and then evaluated some physical properties of this prepared die stone. **Materials and methods** : The values of some physical properties of the prepared die stone in boiling with 30% calcium chloride solution which are water/powder ratio, setting time, and compressive strength were compared with that of three types of gypsum products commercial die stone, Elite type III dental stone and Iraqi plaster. The data were collected , mean and standard deviation were determined. Statistically, (ANOVA) and Dunnett Pairwise Multiple Comparison test were carried out to determine the significant differences at $p\leq 0.05$ **Results**: Results showed that there were no significant differences between the locally prepared die stone and the commercial one at $p\leq 0.05$ in water/powder ratio and setting time values, but it was significant difference in compressive strength. But there are a significant difference between the physical properties of the locally prepared die stone and Elite type III dental stone and Iraqi plaster. **Conclusions:** The results showed the physical properties of the locally prepared die stone approach the physical properties of the commercial product according to the recommendation of ADA for gypsum products.

Key words: Gypsum ,die stone, physical properties

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INTRODUCTION

Gypsum is a very soft mineral composed of calcium sulfate dihydrate, with the chemical formula $CaSO_4.2H_2O$[1]. Gypsum occurs in nature as flattened and often twinned crystals and transparent cleavable masses called selenite. It may also occur silky and fibrous, in which is commonly

called *satin spar*. Also, it may be granular or quite compact [2]. Dentists widely used gypsum products in many dental fields and especially in prosthetic one [3] . The process of manufacturing all classes of gypsum products consist of calcining (dehydration) by heating to expel water constituent [4]. Dehydration is carried out when the gypsum mineral is heated in an open kettle or dehydration in an autoclave under steam pressure and dehydration in boiling 30% calcium chloride solution. The powder obtained by this process is the densest of the types, and described as a high strength dental stone called "Densite" which is also called type IV die stone[5-7].

MATERIALS AND METHODS

Preparation of the local die stone material: The raw gypsum taken from Erbil mountain from the same source that the gypsum factories were taken. This raw were crushed and grinded to a fine particles[8]. Grinding done with the grinding machine (Heazog, Germany).Then sieving the grinded raw gypsum by using sieve mesh No.100 ASTM ((Retsch Test sieve, Germany). A constant amount of this raw material (200gm) mixed with calcium chloride solution in concentration of 30% which has been prepared by taking 30gm of solid $CaCl_2$ dissolved with 100ml of distilled water in Pyrex beaker. The mixture was left on the mantle heater (Electrothermal , U.K) .The mixture was left to boil for one hour[9]. The temperature of the boiling mixture was measured using thermometer and it was ($150C^0$), at this temperature some of the water contained of the calcium sulfate dihydrate ($CaSO_4.2H_2O$) drive off and this lead to conversion to calcium sulfate hemihydrates ($CaSO_4.1/2H_2O$) that cause increase their specific gravity[10]

Good washing of the mixture with boiling distilled water 100°C. The totally washing of the remnant calcium chloride were tested by using of the silver nitrate ($AgNo_3$) as indicator which confirm if there is a remnant chloride that appeared first as a turbidity and then precipitate as a white particles of $AgCl_2$, or not present at all [11] .Then filtration of the mixture using filter paper in Pyrex glass funnel put over Pyrex volumetric flask in hot dry oven at a temperature of 100°C . The calcium sulfate hemihydrate in the presence of 100°C water does not react to form calcium sulfate dihydrate because at this temperature their solubility are the same [6] .

The dryness of the mixture has been done using hot dry oven (Hotbox oven-Gallenkamp ,U.K) at a temperature of 100°C for (4) hour[9] . Then grinding of the dried prepared mass to a very fine particles[6-12] . After that, the tested gypsum product has been sieved by using sieve with mesh number 200. ASTM[13] .

Addition of Additives: This included the retarders and accelerators to control the setting time and the setting expansion of the gypsum products[12,14] .The accelerator used was the potassium sulfate (K_2SO_4) in concentration of 2% ,and Borax ($Na_2B_4O_7.10H_2O$) which is an excellent retarder in concentrations 1%.

Evaluation of Some Physical Properties of the Tested gypsum Product:

Samples of locally prepared die stone compared with other gypsum products which included commercial die stone(Guangzhou, Stone factory. China) Elite dental stone (Zhermack ,Italy) and Iraqi plaster (Al-Ahliya Co. Iraq) .

1.Measuring Water/Powder Ratio (Consistency Test):

In regard to ADA specification No. 25 Modified Vicat Apparatus (MANFREDI, Italy) was used for measuring the water/powder ratio(consistency) [13] . Three hundred (gm) of each type of gypsum products were mixed with of 4% sodium citrate solution(retarder), poured into the mould and then the top of the mould stroked with spatula. The conical plunger of the device cleaned with a moist tissue before each determination, and lowered to the surface of the sample. The scale is read, and then the plunger released quickly. After the plunger has been settled, the scale is read again. The difference in scale reading is the millimeters of penetration. Determinations are made at 7, 8 and 9m from the start of mixing. Three penetrations were to be averaged for each determination. The average of three determinations should be taken as a measure for consistency of each gypsum products, then comparison was made.

2. Measuring of the Setting Time:

According to ADA Specification No.25 the setting time was measured by using a Vicat setting apparatus (Maruto testing machine Co. ,U.S.A) [13] . It is consisted of a frame bearing a 300gm movable rod. One end of the rod has a needle with 1mm in diameter and 5cm in length. Two hundred gm of powder, was mixed with distilled water at correct water/ powder ratio. The mixture is poured in the mould, which was filled and wiped with spatula. The setting time is determined by bringing the tip of the needle into contact with the surface of the material and locking it in position with a thumbscrew. The needle then released and allowed to penetrate the samples at 15sec intervals, beginning from 1 or 2 min prior to the anticipated setting time (usually loss of gloss). After each determination, the needle should be wiped clean with wet tissues and the mould moved to allow the next penetration to be in a new area. This procedure was repeated 5 times for each product and then the mean was calculated.

3.Measurement of the Compressive Strength of the Gypsum Products:

The compressive strength values were determined according to ADA specifications No. 25[13] . A special split moulds were used to prepare cylindrical specimens 20 mm in diameter and 40 mm in length. Gypsum products mixed mechanically with distilled water at correct water/ powder ratio. The prepared mix was poured down the side of the mould retained on a glass plate. The mould then vibrated by a vibrator while being filled to decrease the incidence of porosity formation. The filled mould then covered with a second glass plate which pressed firmly into contact with the top surface of the mould to ensure parallel ends of the samples. The specimens were removed from the split moulds after about one hour from the starting point of mixing and stored in air at, 23C°± 2C° and 50±10% relative humidity.Then the sample was crushed after two hours from the start point of mixing by using Instron Testing Machine (Inc. model CN472, EVANSTON, 111 USA) at a loading rate of 2900 ± 490 N/min (300± 50 Kg/ min) for dental stone .Total number of samples was (20). Five samples for each gypsum products. The compressive strength was determined according to the following formula:

$$\text{Compressive Strength} = \frac{\text{Load (Kg)}}{\text{Area (Cm}^2\text{)}}$$ [15]

RESULTS

The mean and standard deviation of the water / powder ratio of the tested gypsum products are shown in Table (1)

Table (1): The mean and standard deviation of the water/powder ratio of the tested gypsum products

Type of gypsum products	N	Minimum	Maximum	Mean (ml/100g)	± SD
Local Prepared Die stone	5	22.90	23.40	23.1800	0.19235
Commercial Die stone	5	21.70	23.30	22.5100	0.68228
Elite Dental Stone	5	30.10	34.00	32.7000	1.51162
Iraqi Plaster	5	49.20	50.80	50.2000	0.62048

N= number of sample SD= Standard deviation

The results showed that the Iraqi plaster has the higher water/ powder ratio, while the commercial die stone has the lowest value of water/powder ratio and the local prepared die stone has higher ratio than the commercial product but lower than that of Elite dental stone . The results showed that the water/powder ratio of all tested gypsum products are all accordance with ADA specification No.25 for gypsum product [13]. Analysis of variance (ANOVA),Table (2), shows that there are highly significant differences at ($P \leq 0.001$) in the mean value of the water/ powder ratio .

Table (2): Analysis of variance (ANOVA) for levels of gypsum products on the water/powder ratio

Water/powder ratio (ml/100g)	SS	df	MS	F–value	*p*–value
Between Groups	2497.477	3	832.492	1049.636	0.000*
Within Groups	12.690	16	0.793		
Total	2510.167	19			

df= degree of freedom. MS: Mean Square. * Indicated significant difference

Dunnett Pairwise Multiple Comparison results in Table (3) shows that there is no significant difference between the water/powder ratio of local prepared die stone and the commercial die stone.

Table (3): Dunnett Pairwise Multiple Comparison for water/powder ratio of gypsum products

(I) Group	(J) Group	Mean Difference (I–J)	Significance
Commercial Die-stone	Local Prepared Die–stone	0.6700	0.511
Elite Dental Stone	Local Prepared Die–stone	10.1900*	0.000
Iraqi Plaster	Local Prepared Die–stone	27.6900*	0.000

* Indicated significant difference.

The significant difference in the value of the water/powder ratio between the tested gypsum products depend mainly on the physical nature of the gypsum particles including shape, porosity ,size, surface area and the density or specific gravity of the particles [8] .So, the irregular shape and the porosity presence in the (β-hemihydrate) Iraqi dental plaster. These crystals need more water for mixing than any other gypsum products. On the other hand, the more dense and packed and more regular shape crystals (α-hemihydrate) of the locally prepared die stone and commercial die stone possess the lowest value of water/powder than the other gypsum products. These results are supported by Graig *et al* and others [8,14]. The mean and standard deviation of the setting time of the tested gypsum products are shown in Table (4).

Table (4): The mean and standard deviation of the setting time of the tested gypsum products

Type of gypsum products	N	Minimum	Maximum	Mean(min)	± SD
Local Prepared Die stone	5	9.50	12.10	10.9800	1.00598
Commercial Die stone	5	9.80	12.30	11.0400	1.02127
Elite Dental Stone	5	15.10	15.60	15.3400	0.20736
Iraqi Plaster	5	8.50	9.50	8.9800	0.38341

N= number of sample SD= Standard deviation

The result shows that Elite dental stone has the longer setting time, while the Iraqi plaster has the shorter setting time. The results showed that the setting time and compressive strength of all tested gypsum products are all accordance with ADA specification No.25 for gypsum product [13]. Analysis of variance (ANOVA) Table (5).

Table (5): Analysis of variance (ANOVA) for levels of gypsum products on the setting time.

	SS	df	MS	F–value	*p*–value
Between Groups	107.745	3	35.915	63.991	0.000*
Within Groups	8.980	16	0.561		
Total	116.725	19			

df= degree of freedom. MS: Mean Square. * Indicated significant difference

Shows that there are a significant differences at ($P \leq 0.001$) in the mean value of the setting time of the tested gypsum products. Dunnett Pairwise Multiple Comparison results in Table(6)**.**

Table (6): Dunnett Pairwise Multiple Comparison for setting time of tested gypsum products

(I) Group	(J) Group	Mean Difference (I–J)	Significance
Commercial Die–stone	Local Prepared Die–stone	0.0600	0.998
Elite Dental Stone	Local Prepared Die–stone	4.3600*	0.000
Iraqi Plaster	Local Prepared Die–stone	–2.0000*	0.002

* Indicated significant difference.

Shows that there is no significant difference between the setting time of local prepared die stone and the commercial die stone. The difference in the value of the setting time between the tested gypsum products depend on the water/powder ratio. The more water that is used for mixing, the fewer nuclei of crystallization and longer will be the setting time. More water mean longer time for the solution to become saturated and thus for dihydrate crystals to begin to precipitate out [16,17]. This explain the significant difference between the mean value of the setting time of the different tested gypsum products that have significant difference in the mean value of the water/powder ratio as shown in Table (2). The mean and standard deviation of the compressive strength of the tested gypsum products are shown in Table (7) .

Table (7): The mean and standard deviation of the compressive strength of the tested gypsum products

Type of gypsum products	N	Minimum	Maximum	Mean (kg/cm^2)	± SD
Local Prepared Die–stone	5	249.73	251.75	250.6540	0.91615
Commercial Die–stone	5	271.95	278.99	275.2880	2.65534
Elite Dental Stone	5	222.30	229.10	226.0000	2.51197
Iraqi Plaster	5	74.90	76.50	76.0000	0.65574

N= number of sample SD= Standard deviation

The results showed that the Iraqi plaster has the lowest value of compressive strength, while the commercial die stone has the highest value of compressive strength. The results showed that the compressive strength of all tested gypsum products are all accordance with ADA specification No.25 for gypsum product [13]. Analysis of variance (ANOVA) in Table (8).

Table (8): Analysis of variance (ANOVA) for levels of gypsum products on the compressive strength

	SS	df	MS	F–value	*p*–value
Between Groups	120454.61	3	40151.536	10977.751	0.000*
Within Groups	58.521	16	3.658		
Total	120513.13	19			

df= degree of freedom. MS: Mean Square. * Indicated significant difference

shows that are significant differences at (P< 0.001) in the mean value of the compressive strength of the tested gypsum products. Dunnett Pairwise Multiple Comparison results in Table(9).

Table(9): Dunnett Pairwise Multiple Comparison for compressive strength of gypsum products

(I) Group	(J) Group	Mean Difference (I–J)	Significance
Commercial Die–stone	Local Prepared Die–stone	24.6340*	0.000
Elite Dental Stone	Local Prepared Die–stone	–24.6540*	0.000
Iraqi Plaster	Local Prepared Die–stone	–174.6540*	0.000

* Indicated significant difference.

Shows that there is a significant difference between the compressive strength of local prepared die stone and the commercial die stone.

DISCUSSION

The compressive strength of a set gypsum product is related directly to the amount of water used in mixing. The greater the water/ powder ratio, the weaker the product will be [18] . As the particles shape of the commercial die stone and the locally prepared die stone differed from that of the Iraqi plaster and also have lesser water/ powder ratio so they have the highest value of compressive strength. This result come in agreement of the results of Schwedhelm and Lepe [19]. The locally prepared die stone have a compressive strength value lowered than that of the commercial die stone as shown in Table(7). This can summarized to the following causes; Walter [20]stated that during the preparation of the product, it should be regrinding using special grinding machine just before using it to achieve the finest powder crystals which in turn improve the mechanical properties of the product, unfortunately this machine not available in the local market. Also, the equipments that to be used in the steps of the preparation of this gypsum product, were not available in our locality that affect on the quality of the product.The final fact is that the commercial die stone contains extra salts to control the properties of the die stone. It is one of the manufacturer secrets [6].All these above facts made the commercial product possess higher compressive strength than the local product**.**

CONCLUSION

The results showed there is a significant differences between the physical properties of the tested gypsum products .The results showed the physical properties of the locally prepared die stone approach the physical properties of the commercial product according to the recommendation of ADA for gypsum products.

REFERENCES

1. Siadat A and Shahrokhi R. Gypsum products used in dentistry field . *J Prosthet Dent* .2007; 4:24-50.
2. Chaffee NR, Bailey JH, and Sherrard DJ. Dimensional accuracy of improved dental stone and epoxy resin die materials Part II: Complete arch .*J Prosthet Dent*. 1997; 77(2):235-238.
3. Al-Abidi K, Ellakwa A. The Effect of Adding a Stone Base on the Accuracy of Working Casts Using Different Types of Dental Stone. *J Contemp Dent Pract*. 2006;12(7):17-28.
4. Skinner EW, and Phillip, R.W .The Science of dental materials 5th ed.W.B.Saunder Co. Philadephia, USA. 1960; pp:31-57
5. Comb EC and Smith DC. Some properties of the gypsum materials .*Brit. Dent .J*. 1964; 117:237.
6. Graig RG, Hanks CT, Kohn DH, O'Brien WJ, Powers JM, Wagner WC, Wataha JC. Restorative dental materials. 10th ed, Mosby Co. Missouri, USA. 1997; pp: 333-360.
7. Ener S, Bilgen S, Özbayo G. Effect of heat treatment on grindabilities of celestite and gypsum and separation of heated mixture by differential grinding. *Miner Engin*.2004; 17(3): 473-475.
8. Graig RG and Power JM. Restorative dental materials .11th ed Mosby Co. Missouri, USA .2002; pp 635-670,392-404.
9. Al-hamdani SF, Rejab LT and Yahia M. Evaluation of some physical properties of die stone made from local raw gypsum material. MSc. Thesis.College of dentistry. University of Mosul 2009.
10. Doug P. Canadian Minerals . Year book .2005;pp:120-125.
11. Vogel A.L Text-Book of macro and semimicro qualitative inorganic analysis. 4th ed1964; pp:122-135.
12. Mohammed SA. The effect of processing variable on the surface hardness, flow and setting time of gypsum materials. MSc. Thesis, University of Alabama.1983.
13. American Dental Association Specification. Guide to dental materials and devices. 7th ed. 1974-1975; pp: 86-96, 255-260.
14. Graig RG, O'Brien WJ, powers JM. Dental Materials Properties and Manipulation. 6th ed. Mosby Co. Missouri, USA.1996; pp: 183-213.
15. Salem SA, Al- Hadithi KK, and Al-Shakhily GA. The effect of disinfectant solutions 0n some properties of dental stone cast. *Iraqi Dent J*. 1997; 19: 51-70.
16. Anderson JN .Applied dental materials. 4th ed. Blackwell Scientific publication. London UK. 1972; chap.20, pp.157-169.
17. Winkler MM, Monaghan P, Gillber JL, and Lautenschlager EP. Comparison of four techniques for monitoring the setting kinetics of gypsum. *J Prosthet Dent.* 1998; 79(5); 532-536.
18. Philips RW. Elements of dental materials. 4th ed. W.B.Saunder Co. Philadephia, USA. 1984; pp:62.
19. Schwedhelm ER and Lepe X. Fracture strength of type IV and type V die stone as a function of time. *J Prosthet Dent.* 1997; 78(6): 554-559.
20. Walter G. S. Strength and durability of the cast upon its rate of setting and the subsequent plaster of Paris. *J Bone Joint Surg Am*. 1997; 2(4):352-363