The effects of a K$_2$SO$_4$ solution on the surface hardness of gypsum type III

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Abstract. Gypsum type III is commonly used for working models and as a tool for restorations or dentures manufacturing in the laboratory. K$_2$SO$_4$ solution is recommended to be added to gypsum type III because it can accelerate the setting time. The aim of this study was to identify the effects of a K$_2$SO$_4$ solution on the surface hardness of gypsum type III. The surface hardness was tested using a Vickers Hardness Tester with a load of 500 gf. The results were analyzed using a one-way ANOVA. The surface hardness of gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution was higher than the surface hardness of gypsum type III manipulated without K$_2$SO$_4$ but lower than the surface hardness of gypsum type IV. Therefore, the use of a 1.5% K$_2$SO$_4$ solution can increase the hardness of gypsum type III but not enough to make it equivalent to the surface hardness of gypsum type IV.

1. Introduction
Gypsum is a frequently used material in dentistry, and gypsum products in dentistry contain calcium sulfate hemihydrate (Ca$_2$SO$_4$.1/2 H$_2$O) [1]. Calcium sulfate hemihydrate can be modified by various methods, so it can be used for working models, dies, impressions, or silica bonding agents in casting material [2]. A working model is used to make dental restorations, full or partial dentures in the laboratory, whereas dies can be used to make tooth replicas for crowns and bridges [3].

Based on American Dental Association Specification No. 25 and ISO 6873 in 1998, gypsum products in dentistry can be classified into five types: type I (impression plaster), type II (dental plaster), type III (dental stone), type IV (dental stone, high strength), and type V (dental stone, high strength, high expansion) [4].

Gypsum type III is used for making positive impressions such as working models from tooth impressions and as a tool for making restorations or dentures in the laboratory [5]. As a working model, the gypsum must have a good surface hardness in order to be able to withstand the pressure on the surface during restoration or denture manufacture [6]. Gypsum type IV is used for making dies that can be used as tools for making crowns or bridges [1]. The surface hardness of gypsum type III is 11.38 VHN [7], while gypsum type IV has a hardness of 45 VHN [8]. Gypsum surface hardness can be decreased if the gypsum is in prolonged contact with alginate impression material [9]. A decrease in surface hardness value will cause the gypsum surface susceptible to scratches and abrasions [2].

Potassium sulfate (K$_2$SO$_4$) is an effective accelerator for gypsum setting time [1]. A 1.5% concentration of K$_2$SO$_4$ solution is recommended for use with gypsum type III because it can accelerate the setting time without reducing the manipulating time [10]. When calcium sulfate hemihydrate reacts with K$_2$SO$_4$ solution it will form a syngenite compound which becomes the core of
the calcium sulfate dihydrate crystals growth. Syngenite with the chemical formula [K$_2$Ca(SO$_4$)$_2$•H$_2$O] has a higher solubility rate than calcium sulfate dihydrate, so that syngenite crystals are formed faster than calcium sulfate dihydrate crystals, and the growth of crystals with syngenite cores will be faster. Because of that process, a K$_2$SO$_4$ solution can accelerate the gypsum setting time. Also, syngenite molecule is larger than calcium sulfate dihydrate; therefore, there is increased growth of calcium sulfate dihydrate crystals in syngenite, making the intercrystalline space smaller and the crystal structure denser [5]. This crystal structure can affect other properties of gypsum, including the gypsum surface.

Gypsum type IV contains potassium sulfate; therefore, it has higher hardness than gypsum type III [1]. However, gypsum type IV is more expensive than gypsum type III, so the latter is used more often. Because potassium sulfate can form large calcium sulfate dihydrate crystals with a small intercrystalline space, the addition of K$_2$SO$_4$ to gypsum type III could be used to produce models with a higher surface hardness, therefore providing an alternative to gypsum type IV. Thus, this study tested the surface hardness of gypsum type III, gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution, and gypsum type IV.

2. Materials and Methods
Three types of gypsum were tested: gypsum type III, gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution, and gypsum type IV. Two tests were performed: a gypsum setting-time test and a surface hardness test. The specimens were made by stirring gypsum powder with water in a ratio according to the manufacturer’s instructions: 30 ml of distilled water and 100 g of gypsum powder for gypsum type III; 30 ml of a 1.5% K$_2$SO$_4$ solution and 100 g of gypsum powder for gypsum type III made with K$_2$SO$_4$; and 20 ml of distilled water and 100 g of gypsum powder for gypsum type IV. The gypsum type III used was Moldano, which has a composition that includes ammonium chloride, silica, and calcium sulfate hemihydrate [11]; the gypsum type IV used was Fujirock, which contains calcium sulfate hemihydrate, potassium sulfate, trisodium citrate, and potassium hydrogen tetrad [12,13]. The 1.5% K$_2$SO$_4$ solution was made by adding 1.5 g of K$_2$SO$_4$ to 100 ml of distilled water.

A Vicat needle was used to test the effectiveness of the 1.5% K$_2$SO$_4$ solution as an accelerator for the setting time. There were 5 specimens in each test group. The gypsum was manipulated with a gypsum mixer and then put in a 50-ml plastic container. Then, the Vicat needle was used to penetrate the gypsum every 15±1 seconds. The Vicat needle was released repeatedly in different locations on the specimens until the needle penetrated them at a depth of less than 2 mm.

A surface hardness test was performed using a Vickers Hardness Tester. There were 7 specimens in each test group. The gypsum was manipulated with a gypsum mixer and then put in an aluminum mold on the vibrator. The hardness test was performed with a 500-gf load for 10 seconds 5 times in different spots on each specimen. The test was performed at 1 hour, 24 hours, and 7 days after the specimen fabrication. After the indentations were made, the diagonal between the two indentations was measured using the ruler in the microscope, and the results were processed with a Vickers Hardness Tester to obtain the values of the surface hardness. The normality and homogeneity of the data distribution was tested using Shapiro-Wilk test and a test of the Levene statistic. One-way ANOVA was performed to test for a significant difference among the hardness values at 1 hour, 24 hours, and 7 days after gypsum manipulation. Then, a post hoc Bonferroni statistic test was performed to identify the significance of the hardness values at 1 hour, 24 hours, and 7 days after manipulation.

3. Results and Discussion
3.1 Results
The test of the setting time was performed on Group 1 (gypsum type III), Group 2 (gypsum type III manipulated using 1.5% K$_2$SO$_4$), and Group 3 (gypsum type IV). The mean setting times are presented in Table 1.
Table 1. Mean setting times of gypsum type III, gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution, and gypsum type IV

| Group | Setting Time (Mean Value ± SD) |
|-------|-------------------------------|
| (1) Gypsum type III | 10 minutes, 36 seconds ± 18 seconds |
| (2) Gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution | 4 minutes, 56 seconds ± 7 seconds |
| (3) Gypsum type IV | 10 minutes, 3 seconds ± 9 seconds |

As seen in Table 1, the setting time of the gypsum type III was 10 minutes, 36 seconds. When K$_2$SO$_4$ was added to the gypsum type III, the setting time was reduced to 4 minutes, 56 seconds. The setting time of the gypsum type IV was 10 minutes, 3 seconds.

Table 2. Mean values of surface hardness of gypsum type III, gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution, and gypsum type IV

| Group | Surface Hardness Mean Value (VHN ± SD) |
|-------|----------------------------------------|
| (1) Gypsum type III | 12.38 ± 0.10 18.47 ± 0.14 24.04 ± 0.22 |
| (2) Gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution | 16.91 ± 0.12 21.14 ± 0.20 38.84 ± 0.12 |
| (3) Gypsum type IV | 23.87 ± 0.11 31.08 ± 0.22 44.91 ± 0.22 |
| Significance$^a$ | 0.00 0.00 0.00 |

$^a$ p < 0.05: threshold for statistical significance

Based on the results of a Shapiro-Wilk test and a test of the Levene statistic, the data were normally distributed and homogeneous in Group 1 (gypsum type III), so a one-way ANOVA was performed to test for a significant difference among the hardness values at 1 hour, 24 hours, and 7 days after gypsum manipulation. The results showed a significant difference ($p < 0.05$). Then, a post-hoc statistic test was performed to see the significance of the hardness values at 1 hour, 24 hours, and 7 days after manipulation. The results showed that the mean hardness value for gypsum type III without K$_2$SO$_4$ solution, tested at 1 hour, 24 hours, and 7 days after manipulation, has statistically significant difference ($p < 0.05$).

Based on the results of a Shapiro-Wilk test and a Levene statistic test, the data were found to be normally distributed and homogeneous in Group 2 (gypsum type III made with a 1.5% K$_2$SO$_4$ solution), so a one-way ANOVA was performed to test for a significant difference in the hardness values at 1 hour, 24 hours, and 7 days after gypsum manipulation; the results showed a significant difference ($p < 0.05$). Thus, the mean hardness value of gypsum type III manipulated using 1.5% K$_2$SO$_4$ solution had a statistically significant difference. Then, a post-hoc test was performed to see the significance of the hardness values at 1 hour, 24 hours, and 7 days after manipulation. The results showed that the mean hardness of gypsum type III made with a 1.5% K$_2$SO$_4$ solution, tested at 1 hour, 24 hours, and 7 days after manipulation, had a statistically significant difference ($p < 0.05$).

Based on the results of a Shapiro-Wilk test and a Levene statistic test, the data were normally distributed and homogeneous in Group 3 (gypsum type IV), so a one-way ANOVA was performed to test for a significant difference in the hardness values at 1 hour, 24 hours, and 7 days after gypsum manipulation; the results showed a significant difference ($p < 0.05$). Thus, the mean hardness value of gypsum type IV had a statistically significant difference. Then, a post-hoc test was performed to see the significance of the hardness values at 1 hour, 24 hours, and 7 days after manipulation. The results showed that the mean hardness of gypsum type IV, tested at 1 hour, 24 hours, and 7 days after manipulation, had a statistically significant difference ($p < 0.05$).
manipulation; the results showed a significant difference (p < 0.05). Therefore, the mean hardness of gypsum type IV had a statistically significant difference. Then, a post-hoc test was performed to test for a significant difference in the hardness values at 1 hour, 24 hours, and 7 days after manipulation. The results showed that the mean hardness of gypsum type IV, tested at 1 hour, 24 hours, and 7 days after manipulation, had a statistically significant difference (p < 0.05).

3.2 Discussion
Based on the setting-time test, the use of a 1.5% K$_2$SO$_4$ solution with gypsum type III accelerated the setting time from 10 minutes 36 seconds, to 4 minutes 56 seconds. This result accords with previous study about the efficacy of a K$_2$SO$_4$ solution in decreasing the setting time of gypsum type III [10]. The results of that study stated that a 1.5% K$_2$SO$_4$ solution can accelerate the setting time of gypsum type III without disrupting the operator’s manipulating time, because the setting time is still ideal for manipulating gypsum, about 5–7 minutes [10]. When gypsum reacts with K$_2$SO$_4$, ions from the calcium sulfate (Ca$^{2+}$ and SO$_4^{2-}$) and ions from the potassium sulfate (K$^+$ and SO$_4^{2-}$) are released and form syngenite [K$_2$Ca(SO$_4$)2•H$_2$O]. Syngenite becomes the core for the growth of calcium sulfate dihydrate crystals, which will become spherulite. The solubility of syngenite is 2.5 g/L, while the solubility of calcium sulfate dihydrate is 2.1 g/L [5]. That high solubility makes syngenite form faster, so there will be more syngenite cores in the solution. Thus, the crystal growth rate is faster, so the calcium sulfate dihydrate crystals that form spherulite will come into contact with one another faster [5]. Therefore, the gypsum setting time will accelerate [5].

Based on this study, there was an increase in the surface hardness for Groups 1, 2, and 3 when tested at 1 hour, 24 hours, and 7 days after manipulation. One hour after manipulation, Group I (gypsum type III) was in the wet-strength phase and had a surface hardness value of 12.38 VHN. A previous study stated nearly the same results one hour after manipulation, with a hardness of 11.38 VHN [7]. In this phase, gypsum still contains water, so the growth of calcium sulfate dihydrate crystals still occurs, and the hardness value increases after 1 hour [14]. That theory fits with this study, in which gypsum type III in the dry-strength phase, after being left to dry in air with 55% humidity, showed a rise in hardness (to 18.47 VHN). Dry strength is a condition in which most of the calcium sulfate dihydrate solution in the gypsum has evaporated [3]. That evaporation process leaves a residue in the form of calcium sulfate dihydrate particles that bind in between calcium sulfate dihydrate crystals [5]. This causes the intercrystalline contacts to be tighter and increases the hardness value of gypsum type III over 24 hours. After the gypsum in this study was left to dry in air with a 55% humidity for 7 days, the hardness value increased to 24.04 VHN. That is because evaporation was still occurring until the 7-day mark, so there were more residues left compared to the amount left after 24 hours [5]. The residues fill the intercrystalline space and decrease the gypsum porosity. So, the gypsum type III hardness at 7 days was higher than the hardness at 24 hours.

The gypsum type III manipulated using 1.5% K$_2$SO$_4$ solution increased in hardness at 1 hour, 24 hours, and 7 days after manipulation. That increased hardness had the same mechanism as for gypsum type III, but the hardness of gypsum type III manipulated using 1.5% K$_2$SO$_4$ was higher than the hardness of gypsum type III. This was because of the presence of syngenite, which forms when calcium sulfate hemihydrate reacts with K$_2$SO$_4$. Syngenite binds two SO$_4^{2-}$ ions with one Ca$^{2+}$ ion; therefore, syngenite has more ions than calcium sulfate dihydrate crystals. Syngenite has bigger molecules than calcium sulfate dihydrate crystals [11]. Thus, syngenite crystals grow bigger than calcium sulfate dihydrate crystals, and the intercrystalline space becomes smaller, which causes a decrease in gypsum porosity [5]. Because of that, the hardness of the gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution in this study was higher than the hardness of gypsum type III.

The hardness of gypsum type IV also increased after 1 hour, 24 hours, and 7 days after manipulation. The residue left behind by the evaporation of the calcium sulfate dihydrate solution filled the intercrystalline space, so the hardness increased [5]. The hardness of gypsum type IV was higher than the hardness of gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution because gypsum type IV contains 4% K$_2$SO$_4$ [12]. Because the K$_2$SO$_4$ concentration is higher in gypsum type
IV than in gypsum type III, gypsum type IV has more syngenite. Syngenite has a higher solubility than calcium sulfate dihydrate, so syngenite forms faster than calcium sulfate dihydrate [5]. With more syngenite available, the setting time of gypsum type IV will be faster, and manipulation of the gypsum will be difficult [10]. If a retardant is added to prolong the setting time, manipulation will be easier for the operator [5]. The higher amount of syngenite in gypsum type IV causes the intercrystalline space in gypsum type IV to be smaller than in gypsum type III manipulated using 1.5% K$_2$SO$_4$. Because of that, the porosity of gypsum type IV is lower. Thus, the gypsum type IV in this study had a higher hardness than the gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution.

Another study showed that gypsum that has been in contact with alginate impression material for 12 hours has a lower hardness than gypsum that has been in contact for 1 hour [9]. The water content in alginate impression material can interfere with the rehydration process and prolong gypsum’s setting time [1]. Thus, the gypsum surface becomes softer and more susceptible to abrasions and scratches [1]. Also, gypsum’s surface hardness can be decreased if gypsum reacts with disinfectant solutions, because the ions in disinfectant solutions can interfere with calcium sulfate dihydrate crystallization [14]. Therefore, the increase in the hardness of gypsum type III manipulated using 1.5% K$_2$SO$_4$ is expected to overcome the decrease in hardness caused by prolonged contact with alginate or disinfectant solutions. Using K$_2$SO$_4$ in gypsum type III was proven to increase the hardness of gypsum type III, but it was not equivalent to the surface hardness of gypsum type IV. Therefore, gypsum type III manipulated using a 1.5% K$_2$SO$_4$ solution cannot replace the function of gypsum type IV as a material for die making, which requires a material with a high hardness.

4. Conclusion

The use of a K$_2$SO$_4$ solution can increase the hardness of gypsum type III but not enough to make it equivalent to the surface hardness of gypsum type IV.

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