The effects of K$_2$SO$_4$ solution on the compressive strength of dental gypsum type III

T Adeilina, S Triaminingsih* and D J Indrani

Department of Dental Materials, Faculty of Dentistry, Universitas Indonesia, Jakarta, Indonesia

*E-mail: ami_permana@yahoo.com

Abstract. Dental gypsum type III is used as a material for manufacturing working models of dentures. The aim of this study was to identify the effects of the addition of a K$_2$SO$_4$ solution on the compressive strength of gypsum type III. A compressive strength test was performed using a universal testing machine with a crosshead speed of 1 mm/min. The data were analyzed using a one-way ANOVA. The results showed that the compressive strength of gypsum type III with a 1.5% K$_2$SO$_4$ solution added was higher than for gypsum type III alone but lower than the compressive strength of gypsum type IV.

1. Introduction
Dental gypsum type III is used as a material for manufacturing working models of dentures [1]. Working models require a strong material that is not easily fractured. Dental gypsum type III contains powdered particles of calcium sulfate hemihydrate with a prismatic shape and a regular crystal [2]. The powdered particles of calcium sulfate hemihydrate in dental gypsum type IV are more regular than those in dental gypsum type III, so the ratio of water to powder in dental gypsum type IV is lower [1]. Dental gypsum type III has a minimum compressive strength of at least 20 MPa, less than that of dental gypsum type IV, which has a minimum compressive strength of at least 35 MPa [3].

K$_2$SO$_4$ is an effective accelerant for the hardening of gypsum. A 1.5% concentration of K$_2$SO$_4$ solution is the most effective because it is conveniently used by the operator [4]. A K$_2$SO$_4$ solution can accelerate the setting time because when mixed with powdered particles of calcium sulfate hemihydrate, it will form the compound syngenite [K$_2$Ca(SO$_4$)$_2$•H$_2$O]. Syngenite will then become the core of the calcium sulfate dihydrate crystals. Syngenite has a solubility of 2.5 g/L, which is greater than the solubility of calcium sulfate dihydrate (2.1 g/L) [5]. The higher solubility causes syngenite crystals to form faster than calcium sulfate dihydrate, so that the growth rate of calcium sulfate dihydrate crystals with a syngenite core is faster than the growth rate of calcium sulfate dihydrate crystals with a core of only calcium sulfate dihydrate. A syngenite core is larger than a calcium sulfate dihydrate core because syngenite has fewer ions, so the molecule is larger [5,6]. The larger size of the core can cause the calcium sulfate dihydrate crystals to grow larger, thus minimizing the space between them.

Dental gypsum type IV contains K$_2$SO$_4$ salt, which is the cause of its higher compressive strength compared to dental gypsum type III. The higher strength occurs because the space between the calcium sulfate dihydrate crystals is smaller, so the crystal structure of calcium sulfate dihydrate is denser [5]. Thus, a solution of K$_2$SO$_4$ is also expected to increase the compressive strength of dental gypsum type III. Dental gypsum type III with an improved compressive strength could be used as an
alternative to dental type gypsum IV. Therefore, this study measured the compressive strength of dental gypsum type III, dental gypsum type III with the addition of a 1.5% K2SO4 solution, and dental gypsum type IV.

2. Materials and Methods

In this study, the preparation of the specimens began with the amounts of water and powder specified by the manufacturer’s instructions. The Group 1 specimens were made by mixing 100 g of dental gypsum type III powder with 30 ml of distilled water; the Group 2 specimens were made by mixing 100 g of dental gypsum type III powder with 30 ml of a 1.5% K2SO4 solution; and the Group 3 specimens were made by mixing 20 ml of distilled water with 100 g of dental gypsum type IV powder [4,7,8]. The dental gypsum type III that was used was produced by Moldano, and the dental gypsum type IV that was used was produced by Fujirock. The 1.5% K2SO4 solution was made by dissolving 1.5 g of K2SO4 into 100 ml of distilled water.

A test of setting time was done to ensure that a 1.5% solution of K2SO4 could work as an accelerator [4]. The test was performed using a Vicat needle and 5 specimens per group. The setting test began with the production of the specimens in each of the groups. The dental gypsum dough was manipulated using a vacuum gypsum mixer. The dough was then cast into a 50-ml pot and placed under the Vicat needle. The Vicat needle was penetrated with an interval of 15 seconds. The setting test was considered to be finished when the Vicat needle could not penetrate >2 mm into the dental gypsum dough [3].

The compressive strength test was performed using a universal testing machine (UTM). There were 7 specimens in each group. The three groups of dental gypsum specimens were made by mixing water and gypsum powder according to the manufacturer’s instructions using a vacuum gypsum mixer, and the dental gypsum was cast into a stainless steel mold with a diameter of 20 mm and a height of 40 mm. The UTM had a load of 2,500 kgf and a test speed of 1 mm/min. The tests were performed at 1 hour, 24 hours, and 7 days after the production of the specimens.

3. Results and Discussion

3.1 Results

Setting time tests were conducted on Group 1 (dental gypsum type III), Group 2 (dental gypsum type III with a 1.5% K2SO4 solution added), and Group 3 (dental gypsum type IV) specimens. The average setting time are listed in Table 1. The setting time test results showed a difference between the setting time of dental gypsum type III with and without 1.5% K2SO4; the use of K2SO4 reduced the setting time of dental gypsum type III. As seen in Table 1, dental gypsum type III without K2SO4 had a setting time of 10 minutes, 36 seconds; with K2SO4, the setting time was 4 minutes, 56 seconds. Dental gypsum type IV had a setting time of 10 minutes, 3 seconds. The values obtained from the compressive strength tests can be seen in Table 2.

Table 1. Setting time of dental gypsum type III, dental gypsum type III with a 1.5% K2SO4 solution, and dental gypsum type IV

| Group                                              | Setting Time ± SD       |
|----------------------------------------------------|-------------------------|
| (1) Dental gypsum type III                         | 10 minutes, 36 seconds ± 18 seconds |
| (2) Dental gypsum type III with a 1.5% K2SO4 solution | 4 minutes, 56 seconds ± 7 seconds |
| (3) Dental gypsum type IV                          | 10 minutes, 3 seconds ± 9 seconds |
The compressive strength data for Group 2 showed a normal distribution. A test of the Levene statistic showed that the data were not homogeneous, so a Welch correction was made so that the data could be tested with a one-way ANOVA. The comparison of the average compressive strengths in Group 1 at the three different time points showed a significant difference among the average strengths of the 24-hour specimens (p = 0.00). There was also a significant difference between the average strengths of the 1-hour and 7-day specimens (p = 0.00) and between the 24-hour and 7-day specimens (p = 0.00). A Shapiro-Wilk normality test of the data for Group 2 showed a normal distribution. A test of the Levene statistic showed that Group 2 had homogeneous data. A one-way ANOVA test showed a significant difference in the average compressive strengths among the three different time points (p = 0.041). A post-hoc Bonferroni test was conducted to examine the results in more detail. For Group 2, there was no significant difference between the average compressive strengths of the 1-hour and 24-hour specimens (p = 0.181), between the 1-hour and 7-day specimens (p = 0.052), or between the 24-hour and 7-day specimens (p > 0.05).

A Shapiro-Wilk test showed that the compressive strength data for Group 3 had a normal distribution. A test of the Levene statistic showed that the strength data were homogeneous. A one-way ANOVA was performed to test for strength differences among the three time points; a significant difference was found (p = 0.002). A post-hoc Bonferroni test was performed to examine the results more closely. For Group 3, there was a significant difference between the average compressive strengths of the 1-hour and 24-hour specimens (p = 0.005), between the 1-hour and 7-day specimens (p = 0.005), and between the 24-hour specimens and the 7-day specimens (p < 0.05). Another set of comparisons was made among the 1-hour specimens from Groups 1, 2, and 3. A Shapiro-Wilk test showed a normal distribution of the data. However, a test of the Levene statistic showed that the data distribution was not homogeneous. A Welch correction was used to correct the data so that they could be tested with a one-way ANOVA, which showed a significant difference among the compressive strengths of the three groups (p = 0.00). A post-hoc Games-Howell test showed a significant difference in the compressive strengths of the 1-hour specimens between Groups 1 and 2 (p = 0.024), between Groups 1 and 3 (p = 0.00), and between Groups 2 and 3 (p = 0.00).

The data for the 24-hour specimens from Groups 1, 2, and 3 had a normal distribution. However, the Levene test statistic showed that the data were not homogeneous, so a Welch correction was performed so that the data could be tested with a one-way ANOVA. There was a significant difference among the average strengths of the 24-hour specimens in Groups 1, 2, and 3 (p = 0.00). The results of a post-hoc Games-Howell test showed that there was no significant difference between the average compressive strengths in Groups 1 and 2 (p = 0.175). However, there was a significant difference between the average compressive strengths in Groups 1 and 3 and between Groups 2 and 3 (p = 0.00 for both). A Shapiro-Wilk test showed that the data from the 7-day specimens in Groups 1, 2, and 3 had a normal distribution. A test of the Levene statistic showed that the data were not homogeneous, so a Welch correction was performed so that the data could be analyzed with a one-way ANOVA. There was a significant difference among the average compressive strengths in Groups 1, 2, and 3 (p =

### Table 2. Compressive strength of dental gypsum in the three specimen groups

| Specimen groups                      | Compressive strength (MPa) ±SD |
|--------------------------------------|--------------------------------|
| (1) Dental gypsum type III + distilled water | 20.33 ± 0.39                 |
| (2) Dental gypsum type III + 1.5%K₂SO₄ solution | 21.96 ±0.33                  |
| (3) Dental gypsum type IV + distilled water | 37.94 ±1.28                  |
|                                      | 22.01 ±0.36                  |
|                                      | 23.31 ±0.35                  |
|                                      | 44.82 ±1.3                   |
|                                      | 29.05 ±1.06                  |
|                                      | 23.72 ±0.49                  |
|                                      | 44.85 ±1.3                   |
The arms of the calcium sulfate dihydrate crystals. The arms will grow in all directions of the storage of the dental gypsum. Syngenite, which becomes the core of the calcium sulfate dihydrate crystals. Syngenite has a high solubility (2.5 g/L) compared to calcium sulfate dihydrate (2.1 g/L). The crystal growth rate of calcium sulfate dihydrate with a syngenite core is faster than the crystal growth rate of calcium sulfate dihydrate with a core of calcium sulfate dihydrate, because a nucleus of syngenite is formed faster. This core is the origin of the formation of the arms of the calcium sulfate dihydrate crystals. The arms will grow in all directions, following the form of the core, so that there will be contact between the crystals; the contacts accelerate the hardening of the dental gypsum [5].

Tests of the compressive strength of dental gypsum type III made with distilled water were performed at 1 hour, 24 hours, and 7 days after the production of the samples. The results showed an improvement in compressive strength over time. The test of the wet strength of gypsum type III, which took place 1 hour after the specimen production, showed a compressive strength of 20.33 MPa. At this stage, the calcium sulfate dihydrate crystals are forming with a nucleus of calcium sulfate dihydrate. The test of dry strength, 24 hours after the specimens were made, showed an increase in the value of the compressive strength to 22.01 MPa. This is because during the storage of the dental gypsum specimens, the water between the crystals evaporates, causing a calcium sulfate dihydrate residue to form. This residue is deposited between the calcium sulfate dihydrate crystals, causing the bonds to become stronger. Therefore, there is an improvement in the compressive strength. After 7 days, the compressive strength increased to 29.05 MPa. This is because when dental gypsum is left to dry in the open air, which has a moisture content of 55%, evaporation still occurs, causing more calcium sulfate dihydrate residue to affix to the calcium sulfate dihydrate crystals [5]. The more excess water that evaporates, the more the compressive strength increases.

The compressive strength of dental gypsum type III with an added solution of 1.5% K2SO4 was tested at 1 hour, 24 hours, and 7 days after the production of the specimens. At 1 hour, the compressive strength was 21.96 MPa. At this stage, the K2SO4 solution causes the formation of syngenite, which becomes the core of the calcium sulfate dihydrate crystals. Syngenite has a higher solubility than calcium sulfate dihydrate, so the syngenite nucleus is more quickly formed. The faster core formation causes more calcium sulfate dihydrate crystals to form so that the crystal structure becomes denser. In addition, the syngenite nucleus has a large size because it contains many syngenite molecules. A larger core causes the arms of the calcium sulfate dihydrate crystals to become larger and minimize the space between the calcium sulfate dihydrate crystals. In testing the dry strength 24 hours after the specimens were made, the compressive strength was found to be 23.31 MPa. This increase in the value of the compressive strength is not significant because the space between the calcium sulfate dihydrate crystals is small. The compressive strength of the 7-day specimens (23.72 MPa) was not significantly higher than that of the others. This is expected, because the water in the calcium sulfate dihydrate has evaporated at 24 hours after the specimen production. At 7 days, there is no more water to be evaporated, so the strength tends to remain constant.
At 1 hour after manipulation, the compressive strength of the dental gypsum type III made with K2SO4 was significantly higher than the compressive strength of the dental gypsum type III made with distilled water. This is due to the formation of syngenite in the gypsum with K2SO4. Syngenite can accelerate the growth rate of calcium sulfate dihydrate crystals. In the dry-strength (24-hour) test, the strength of gypsum type III with K2SO4 was not significantly higher than that of the gypsum type III made with distilled water. This is because the space between the calcium sulfate dihydrate crystals is smaller in the gypsum made with K2SO4. Thus, there is less residual calcium sulfate dihydrate in between the calcium sulfate dihydrate crystals, so the process of evaporation of the calcium sulfate dihydrate solution does not have a great impact on the compressive strength. In addition, for the 7-day specimens, the strength of the dental gypsum type III manipulated with K2SO4 was lower than the strength of the dental gypsum type III made with distilled water. This is expected that when gypsum is made with K2SO4, the water evaporates within 24 hours, whereas in regular gypsum, some water still remains on day 7.

The compressive strength of the dental gypsum type IV at 1 hour was 37.94 MPa. This is because dental gypsum type IV has a high concentration of K2SO4 (4%) [4]. A high concentration of K2SO4 causes a higher number of syngenite cores to form, so that the crystal structure of the calcium sulfate dihydrate will be denser. The compressive strength of gypsum type IV at 24 hours (44.82 MPa) was significantly greater than the strength at 1 hour. A significant increase is expected because the concentration of K2SO4 is high, which causes the syngenite cores to continue to grow after the 1-hour test. This is because the syngenite nuclei will continue to grow until some of the K+ ions are used in the formation of calcium sulfate dihydrate crystals [6]. However, the compressive strength of the dental gypsum type IV at 7 days (44.85 MPa) was not significantly higher than the others. At this stage, the high concentration of K2SO4 causes there to be less space between the calcium sulfate dihydrate crystals so that there is less residual calcium sulfate dihydrate solution between the crystals. With little solution present, the process of evaporation does not significantly increase the compressive strength of the dental gypsum type IV 7 days after it was made.

Dental gypsum type IV had a higher compressive strength than the dental gypsum type III made with K2SO4. This is due to the high concentration of K2SO4 in dental gypsum type IV (4%) which is added by the factory to reduce the expansion of dental gypsum. The high concentration of K2SO4 in gypsum type IV also causes more syngenite cores to form [9], leading to a greater number of syngenite cores, a higher production of calcium sulfate dihydrate crystals, and a reduction in the space between the calcium sulfate dihydrate crystals. Based on this study, the use of a 1.5% K2SO4 solution can increase the compressive strength of dental gypsum type III at 1 hour after manipulation. However, the compressive strength of dental gypsum type III manipulation with K2SO4 is not as high as that of dental gypsum type IV. This is expected, because a concentration of 1.5% is not able to significantly improve the crystal density of calcium sulfate dihydrate. Therefore, due to its lower compressive strength, dental gypsum type III made with 1.5% K2SO4 cannot functionally replace dental gypsum type IV.

4. Conclusion
A 1.5% K2SO4 solution improves the compressive strength of dental gypsum type III on 1 hour after manipulation. However, dental gypsum type III manipulation with 1.5% K2SO4 cannot be an alternative to dental gypsum type IV, when viewed from the compressive strength.

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