Effect of shelf life on compressive strength of type IV gypsum

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Abstract. Type IV gypsum, as a dental material for an indirect restoration’s working model, should have strength and abrasive-resistant properties. These properties depend on the product’s shelf life and its proper storage, which sometimes are easily missed by sellers. The aim of this research was to observe the effect of shelf life on the compressive strength of type IV gypsum with different production dates. Twenty cylindrical specimens were separated into two groups with different production dates and tested with a universal testing with the crosshead speed of 1 mm per minute and a load of 2,500 kgf. The data were analyzed with independent t-tests. There was a significant difference ($p<0.05$) in the compressive strength between the two groups with an increase in compressive strength seen in the gypsum that was stored longer.

1. Introduction
Advances in dental materials technology that can restore speech and mastication functions, and even aesthetic aspects are why dental care is currently interested in this community of products. With the development of technology and material dentistry, and the aesthetic needs of the community, more alternative treatments can now be offered to patients. Treatment to restore functions of the teeth and mouth are not only concerned with direct restorations, such as filling materials, but also indirect restorations, such as veneers, bridges (denture bridges), and crowns. The success of crown restorations cannot be separated from the manufacturing process. One of the procedures performed in crown restorations is a modelling job or die cast. A die cast is a replica model of the patient's teeth made of supporting material, such as dental gypsum [1]. Type IV gypsum is a high-strength dental stone that has more compressive strength than other types of gypsum, and it has a hard surface, making it resistant to abrasion and suitable for the manufacture of a die cast [1]. This does not affected by the coping crown wax carving procedure, thus, causing no harm to either the dentist or patient [2,3].

Gypsum products marketed in Indonesia are typically imported from abroad, and from sites that are generally in non-tropical climates. The exposure of these materials to Indonesia's tropical climate, which can affect gypsum’s properties, can occur during transportation or storage of the materials in dental stores. In addition to storage requirements, special attention needs to be given to the appropriate temperature and relative humidity, the types of packaging, and storage time. These factors can be considered as indicators of whether type IV gypsum is still useable and if its quality is sufficient for its intended use in the manufacture of die casts.

Shelf life is the time specified by the manufacturer in which the material can maintain its quality and nature and can still be used as intended. Thus, shelf life is influenced by several factors including temperature, humidity, and the current state of delivery [4,5]. Temperature and relative humidity levels are recommended for the storage of dental gypsum according to the ISO 6873: 1998, these...
levels are 23±2 °C and 50±0%, respectively. However, Indonesia has a temperature and humidity above the standards, 30°C and 70%, respectively [6,7]. If a material’s quality is already decreasing, the material’s shelf life has expired, even if the actual expiration date has not been reached. Several studies have shown that physical, mechanical, and chemical materials undergo various changes and show decreases in compressive strength due to long storage times and unfavourable storage conditions that are not meeting the suitable standards [8,9]. However, previous research suggests that, in some materials, time can improve a material’s qualities [5]. Thus, a material’s compressive strength may be influenced by several factors.

2. Materials and Methods
This study was performed in an experimental research laboratory. We used 20 pieces of type IV gypsum specimens (GC Fujirock EP), which were divided into two groups based on production dates. Type IV gypsum specimens were formed into cylindrical shapes with a 20-mm diameter and a 40-mm height, which was obtained from a split mold made from stainless steel in accordance with ISO 6873: 1998 and ADA Specification No. 25 [6,10]. Before pouring the gypsum into the mold, the gypsum sample was obtained by mixing 200 g of powder with 40 ml of distilled water. The mixture was left for 10 seconds and mixed by hand for another 60 seconds for 75 rounds until it was homogeneous and creamy.

The dough was poured into mold casts that had been coated with Vaseline. Below the mold there was a glass plate, and vibration was provided to reduce any air bubble formation. The glass plate closed until it contacted the upper surface of the mold. After all the molds were filled with gypsum, the surface of the glass plate was given a load to remove the excess batter. The gypsum hardened for 45 minutes after manipulation and was then removed from the split mold. The specimens were left undisturbed for 15 minutes before testing.

Specimens were tested one hour after manipulation with a universal testing machine (Shimadzu AG-5000, Japan) with a load of 2,500 kgF and a crosshead speed of 1 mm per minute. When the specimens fractured, the force shown on the screen was recorded. Testing with a universal testing machine can be seen in Figure 1. The compressive strength was calculated in units of kgF/mm² and then converted to units of megapascals (MPa) using the formula:

\[
\text{Compressive strength} = \frac{\text{load (kgF)}}{\text{area (mm}^2\text{)}} \times 9,806 \text{ MPa}
\]

Figure 1. The test of a gypsum specimen in a universal testing machine.

The calculation results obtained with this formula were the compressive strength values. These values were compared with the compressive strength of both the GC Fujirock EP product, which is 53 MPa (according to the GC Europe product brochure in 2013), and the standard for ISO 6873: 1998, which is 35 MPa. Statistical tests were performed with SPSS, which was used to test the Shapiro-Wilk
normality and homogeneity of variance between groups. Having obtained the values of the normal distribution and homogeneity, the means of the two groups were tested statistically with two different test average unpaired \( t \)-tests (independent \( t \)-test) to determine the significance of the differences between groups, with a confidence interval (\( \alpha \)) of 0.05.

3. Results and Discussion

3.1 Results

Table 1 shows the results of the surface roughness value on the composite resin veneer specimens before and after brushing. Table 1 shows the changes in the surface roughness values of the composite resin veneer in each variable subgroup. In subgroup A, the control group, which was brushed without a toothpaste medium, the surface roughness increased from 0.30±0.05 µm to 0.32±0.00 µm after the first 5,000 strokes brushing session and to 0.33±0.00 µm after the second brushing session. Based on the results, the mean surface roughness of the composite resin veneer in the control group (subgroup A) increased from ∆Ra=0.02 µm after the first brushing session to ∆Ra=0.03 µm after the second brushing session.

|                      | Average compressive strength (MPa\(\pm\)SD) |
|----------------------|---------------------------------------------|
| Group I              | 28.93±2.43                                  |
| Group II             | 38.66±3.2                                   |
| Minimum compressive strength value (ISO 6873:1998) | 35                                           |
| GC factory default values | 53                                           |

Table 1 shows that there were differences in the compressive strength of type IV gypsum with different production dates and the comparison with the standard ISO 6873: 1998 and GC factory standard. The compressive strength of type IV gypsum in group is 28.93±2.43 MPa. However, type IV gypsum had a compressive strength of 38.66±3.20MPa.

Table 1 shows there are differences in the values of groups I and II, and also when those values are compared with the compressive strength minimum standards for ISO 6873: 1998. Group I did not meet the minimum standards of the compressive strength set by ISO 6873: 1998, while group II met the standards. However, both groups failed to reach the compressive strength standard of the GC factory. The test results in this study were analyzed using unpaired \( t \)-tests (independent \( t \)-tests) to determine if there was a significant difference in the test group values. Based on the statistical test results, the ratio between the average value of the gypsum in group I and group II showed a significant value of 0.000 (\( p<0.05 \)). This shows that there is a significant difference between groups I and II, suggesting that a longer time after production increases the material’s compressive strength.

3.2. Discussion

The important function of type IV gypsum for modeling work requires that it must be strong and abrasion resistant. Therefore, the nature of these forces need to be considered properly, and this study was conducted to determine if changes in the compressive strength of type IV gypsum are in line with increasing storage times (shelf life). Specimens used in this study were type IV gypsum from GC Fujirock EP, and this brand had good packaging, was sealed, and labeled appropriately on the packaging container. The packages contained information concerning the water/powder ratio, recommended manipulations, expiration dates, and details on the nature of the gypsum, such as setting
time and compressive strength. In this study, group I was type IV gypsum within 10 months after the production date. The second group of type IV gypsum, with the same trademark, within 2 years 3 months after the production date. Both packages indicated recommended usage dates for using the gypsum after the production date, and the packages were still in good condition, tightly closed, and had never been opened.

The method of making specimens during the gypsum manipulation was by using distilled water, as recommended by the factory and ADA Specification No. 25. Studies have shown that the use of distilled water for mixing the powder during manipulation will produce gypsum with optimal strength [11]. In this study, group II had the same consistency and flow as group I. Compressive strength is influenced by several things, such as the ratio of water/powder, manipulation and spatulation, mixing procedures, relative humidity of the room, and the size of calcium sulfate hemihydrate particles [5,9,11]. The compressive strength of the test materials did not meet the standard ISO 6873: 1998, specification ADA No. 25, and the GC factory standard, allegedly because of manipulation procedures that were not in accordance with the manufacturer's recommendations. Printed on the packaging, the manipulation recommendation is to hand-mix for 15 seconds and vacuum-mix for 45 seconds, while the ADA Specification No. 25 recommends mixing by hand up to 120 rpm for 1 minute. In this study, the manipulation was done by the hand-mixing method at 75 rpm for 1 minute, meaning there are spatulation rounds as much as 75 times for 1 minute. Hand-mixing methods were due to the unavailability of a vacuum-mixing tool in the laboratory, and the difficulty of mixing dough for low flow, considering the ratio of water/powder used with small and closely with the manufacturer's recommendations, namely 0.20.

Different manipulation methods can affect the compressive strength because hand-stirring produces a dough that is not a homogenous as that made with an automatic machine. Previous research has stated that vacuum-mixing, or stirring the vacuum, will automatically increase the compressive strength and surface hardness compared to hand manipulation because it produces a more homogenous dough with less porosity and there is a decreased trapping of air bubbles [12,13].

Other factors affecting compressive strength are hemihydrate particles of calcium sulfate powder particles [5]. The α-calcium sulfate hemihydrate particles are small and finer than the particles in the powder dental plaster, which increase porosity, or cavities, between the small particles [14]. Temperature and humidity when testing was controlled at 24.98±0.64°C and 55.17±1.47%, respectively (still within the standard ISO 6873: 1998 and ADA Specification No. 25). This was done to reduce the bias compressive strength values obtained during testing, considering the calcium sulfate hemihydrate crystals are hygroscopic, or bind water in the environment.

Table 1 also shows that there was an increase in the compressive strength of type IV gypsum in group II, or the group with further from the production date, thus, closer to the expiration date. This may have been caused by moisture exposure that occurred during storage at the dental supplier. Storage conditions in the dental supplier warehouse without air conditioning can cause moisture contamination and may result in the exposure of moisture or water in the environment. Although the gypsum was in sealed packaging, packaging products made of polymers or plastics may have degraded during storage, and the absence of aluminum packaging that encloses the calcium sulfate hemihydrate powder exposes hemihydrate powder to moisture. Packaging that can protect from humidity, and tends to be moisture proof, is generally made of metal [2]. Calcium sulfate hemihydrate is hygroscopic and adds to the mass of the particulate calcium sulfate hemihydrate [15]. The addition of this mass is due to the transformation of hemihydrate into dihydrate. This initial conversion forms an inter-crystalline premature bond and ultimately allows for the formation of the gypsum strength. Forms of α-calcium sulfate hemihydrate are smooth with low porosity, and the distance between the small crystals allows for the easy establishment of inter-crystalline relationships.

In the present study, the compressive strength of type IV gypsum in group I did not meet the standards of ISO 6873: 1998, and neither group reached the standard value for the compressive strength of the GC factory. This suggests that the two products from a respected manufacturer with an expensive price and with containers that looked good may have experienced a loss of quality. Thus,
there is no guarantee for an adequate compressive strength value (up to the minimum standard for ISO of 35 MPa). However, the gypsum in group II, which had a compressive strength higher than group I, may have had a higher hemihydrate powder quality at the time of production. This is difficult to determine since an investigation at the time of production was not done. Under the terms of the minimum value of the standard ISO 6873: 1998, the gypsum in group II could still be used because it exceeded the standard value. However, group I gypsum could not have been used because the gypsum had a compressive strength less than the ISO standard and would be at risk for fracture, distortion, and abrasion during the wax carving procedure which can affect the quality of the subsequent procedure resulting in less optimal restoration products.

4. Conclusion
Shelf life or differences in storage times affect the compressive strength of type IV gypsum. The compressive strength of type IV gypsum changed over a long storage period. This study showed that type IV gypsum can still be used even when its approaching 8 months of the expiration date because the compressive strength values still meet the standards of ISO 6873: 1998. However, this applies only if the storage conditions are good and the packaging has remained sealed before it was first opened. Further research is needed regarding the properties of gypsum approaching the expiration date with regard to the condition of the container and whether it has remained sealed and not been previously used. Further studies are needed to perform manipulation of the procedures as recommended by the factory, which can produce a gypsum dough more homogeneously and with an optimum compressive strength value.

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