

Effect of shelf life on compressive strength of zinc phosphate cement

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Abstract. Usage of zinc phosphate cements with no account of the shelf life left before the expiry date can affect its compressive strength. The aim of this study is to determine the different compressive strength values of zinc phosphate cement with different shelf lives before expiry. Three groups of zinc phosphate cement (GC Elite cement 100) with different expiry dates were tested for compressive strength using a universal testing machine (crosshead speed 1 mm/min: load cell of 250 kgF). The results showed that there was a significant difference ($p < 0.05$) between the compressive strengths of zinc phosphate cement in group III (2 months before expiry date), group I (2 years and 5 months before expiry date), and group II (11 months before expiry date). It can be concluded that there is a significant decrease in compressive strength of zinc phosphate cement near its expiry date.

1. Introduction

Patient's visits to dentists can be divided according to their motivation: whether to get preventive or curative treatment [1]. Curative treatment, including restorative treatments, include rehabilitative treatment to regain mastication ability or speaking function, or even to enhance appearance. For these, mainly restorative treatments, dental cement is required. One of the most common cements used is zinc phosphate cement. It is a luting cement, used to adhere metal to the dental surface as the basis for restoration. Zinc phosphate cement is widely used in dentistry because of its thermal conductivity which is almost equal to tooth enamel but less than metal, and has thermal insulation properties for metal restoration. Moreover, zinc phosphate cement is quite a strong cement so it can be used in regions requiring high compressive strength or in a long span prosthesis [2-5].

Zinc phosphate cement, packaged in the form of powder and liquid, requires special care during storage. However, the reality is, because zinc phosphate cement is used so frequently it is not well stored. Zinc phosphate cement which is almost beyond its shelf life or close to its expiry date, as assigned by the manufacturer, is still frequently traded and used by dentists. Some of these dental materials are sold cheaply with big discounts. Even with these discounts, dentists frequently miss the fact that the products have expired, because they do not see the expiry dates of the products they are buying. Moreover, dentists frequently buy a lot of zinc phosphate cement at one time and do not finish using all the cement until it is close to its expiry date. As well as expiry dates, dentists needed to pay attention to shelf life. Shelf life is the storage time limit of a product within which it is still fit for use with the expected results, with no property changes or deterioration. For a product with a limited shelf life, the expiry date is usually marked on the packaging [6]. If a product is used that has decreased



physical or mechanical properties, because it is beyond its shelf life, this will affect the quality of restoration and the patient's satisfaction [7].

According to Hondrum [8], the mechanical properties of dentistry cement are important to support clinical success; the longer storage time before use can have a major effect on its properties. Hondrum mentioned, that shear strength and compressive strength of some luting cements can decrease with increasing length of storage [8]. Meanwhile, Sinaga [9], mentioned that type II glass ionomer cement has an increased hardness score if the shelf life is exceeded. However, the increased hardness could be the result of the cement becoming brittle with decreased quality [9]. Dental materials have to be able to bear the load of muscle tension mainly from mastication, and in patients with parafunctional habits like bruxism. The main forces in the oral cavity are compressive, shear, tensile, and torsion [10]. The most common force in mastication is compressive strength. Okazaki and Kamposiora in the journal of Rosenstiel *et al.* [11] about luting cement mentioned that cement that functions well over a long life span should have adequate bearing strength and not fracture. One of the properties used to predict this strength, in clinical use, is a compressive strength test [11]. This research aimed to analyze the different compressive strength scores of zinc phosphate cement with different storage times, before the expiry date, and to measure how much the compressive strength score increased or decreased.

2. Materials and Methods

The material used in this research was Elite brand 100 zinc phosphate cement produced by the GC Corporation, Japan. The material condition was zinc phosphate cements with varying lengths of storage time that had not exceeded the expiry dates on the packages. The zinc phosphate cement material was new, sealed, and had never been used. The material was chosen according to the product's specification given as: (1) LOT number: the first two numbers are the year of production; the next two numbers are the month of production; and last three numbers are the batch number; (2) length of storage time, according to the manufacturer's instruction: three years after the production date; (3) Expiry date: the first four numbers are the year of expiry. The zinc phosphate cement was divided into three groups: (I) 2 years 5 months; (II) 11 months; (III) and 2 months before the expiry date, during the research (table 1).

Table 1. Zinc phosphate cement group specifications

LOT Number	Production Date	Expiry Date	Period Before Research Occurred
1501051	February 2015	February 2018	2 years 5 months before expiry date
1309011	September 2013	September 2016	11 months before expiry date
1212271	December 2012	December 2015	2 months before expiry date

In this research, 30 specimens of zinc phosphate cement cylinders were formed, 6 mm in height and 4 mm in diameter, using a stainless steel split mold. The research was performed according to the ISO 9917:1991 standard [12]. The room temperature during the manipulation process was $23 \pm 1^\circ \text{C}$ with an air density of $50 \pm 10\%$. The powder to liquid ratio required was 3:1, which was three drops of liquid and 1 scoop of powder, using scoop number 3, according to the manufacturer's measurement instructions. Mixing was done according to the manufacturer's instruction, which was to use a mixing slab of thick glass and a stainless steel cement spatula. The total time needed to manipulate the liquid and powder was 60–90 seconds. The working time for the cement was 3–4 minutes from the initial mixing. The final consistency should be, such, that the cement can be lifted by the spatula, pulled into a long, thin layer and then gently cut back into the gathered cement. After manipulation, the specimen was measured to determine its diameter, and then immersed in aquades for 24 hours at 37°C . Then, the specimen's compressive strength was tested using a universal testing machine with a crosshead speed of 1 mm/min and a load of 250 KgF. When the specimen fractured, the force at the testing tool was noted and calculated with the formula:

$$C = \frac{4p}{\pi \times d^2}$$

where, C is the compressive strength (MPa), p is the maximum force (Newton), and d is the specimen diameter (mm).

3. Results and Discussion

3.1 Results

Compressive strength testing of zinc phosphate Elite 100 Cement (GC Corporation, Japan) was done in three groups. These groups were divided according to the length of storage time before the expiry date written on the packaging. Each group consisted of ten specimens. The first group was a control group with two years and five months left before the expiry date. This group was analyzed during September, 2015. The second and third groups were zinc phosphate cements that had eleven months and two months, respectively, before expiry. These two groups were analyzed during October, 2015. The results of the compressive strength testing, using the universal testing machine (Shimadzu AG-5000E), are shown table 2.

The group means (table 2) showed that the compressive strengths of groups II and III were less than group I (control). The zinc phosphate cement groups which were closest to their expiry dates had the lowest compressive strengths (figure 1). The data means were analyzed using a one-way analysis of variance (ANOVA) test to determine the significance of the different compressive strength scores from the zinc phosphate cement samples with different expiry dates.

Table 2. Compressive strength mean scores of the three groups of zinc phosphate cement

Group name	Number of Specimens	Compressive strength mean (MPa)
I	10	67.49 ± 5.49
II	10	66.84 ± 8.53
III	10	57.24 ± 5.43
ISO Standard	-	70
ADA Standard	-	75

Note:

Group I: Zinc phosphate cement with expiry dates in February, 2018, or two years and five months of storage time left before expiry.

Group II: Zinc phosphate cement with expiry dates in September, 2016, or eleven months of storage time left before expiry.

Group III: Zinc phosphate cement with expiry dates in December, 2015, or two months of storage time left before expiry.

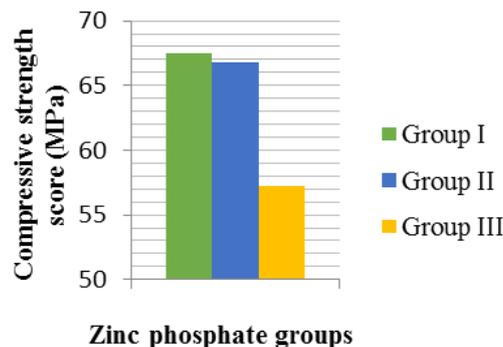


Figure 1. Compressive strength score graphic for zinc phosphate cement

Table 3. ANOVA test results for the three groups of zinc phosphate cement

Specimen group	Specimen group	Sig.	Information
I	II	0.829	Not significantly different
	III	0.002	Significantly different
II	I	0.829	Not significantly different
	III	0.003	Significantly different
III	I	0.002	Significantly different
	II	0.003	Significantly different

The analysis also yielded a least significant difference (LSD) of $p > 0,05$ (table 6). The ANOVA result showed that group III had significantly different scores compared to Groups I and II. This significant score was 0.002 and 0.003 ($p < 0.05$). Meanwhile, group I and II scores were not significantly different at 0.829 ($p < 0.005$).

3.2 Discussion

This research used zinc phosphate cement (Elite Cement 100 brand from GC Corporation, Japan). This material consisted of powder and liquid that respectively had storage lengths before expiry, as written on the packaging, of: two years and five months; eleven months; and two months. The materials used were new, had never been used, and were well sealed. The result was, that there was a significant difference between the three groups of cement. The zinc phosphate cement with a storage length of two months, before expiry, had different compressive strengths compared to the zinc phosphate cements with storage lengths of two years and five months, and eleven months before expiry. The three specimen groups had compressive strengths below the ISO 9917:1991 standard of 70 Mpa. The results for each group were: (I) 67,49 MPa; (II) 66.84 MPa; and (III) 57.24 MPa. This may have been caused by the porosity of the manipulated specimen. This statement fits with Safwat [13] and Fleming et al [14], who stated that the ideal manipulation condition rarely occurs, which is caused by environmental factors (temperature and density) and manipulation (technique and manipulation time). That research also explained that 25% of manipulated zinc phosphate cement had scores below 40 MPa [13,14]. According to Hondrum [8], decreased compressive strength occurs, in zinc phosphate cement, because the liquid component fails to ionize during the setting reaction, due to loss of the water component [8]. Zinc phosphate cement is a water based cement containing 30–55 % liquid. The water in the liquid functions as an acid control for ionization, which effects the setting reaction [3,5].

Water loss could happen because of evaporation of the cement's liquid component. This should be avoided because water is an important component of zinc phosphate cement. If evaporation occurs, the acid concentration of the liquid increases. Evaporation changes the acid to water ratio and an acidic powder could reduce the stability of the liquid component, which could affect the mechanical, physical, and chemical properties of the zinc phosphate cement [15]. During the manipulation process, a dental practitioner should avoid the possibility of water evaporation. This could occur if the water tube has been opened repeatedly, or if the powder and the liquid have been out of the bottle but without immediate manipulation. Zinc phosphate cement, being a water based cement, is hygroscopic and has the ability to attract water molecules from surrounding moist or wet environments. It also easily loses water in dry conditions, if the package has been opened [15-17]. Evaporation is a phenomenon of liquids. It occurs when a liquid molecule has enough kinetic energy to separate from a liquid. This phenomenon is affected by temperature; the higher the temperature the higher kinetic energy available. This can cause evaporation to happen quickly [18,19].

The zinc phosphate cement used in this research was a new and sealed product. However, inappropriate temperature during storage could trigger changes in the liquid composition of the cement. This could be caused by improper cement storage, not in line with the manufacturer's instructions. The manufacturer's suggested storage temperatures are between 4–25° C. In reality, the material is frequently stored in rooms above 25° C with no air chillers. Even though it looks like no

liquid has evaporated, evaporation can happen from the liquid surface in the sealed tube. Zinc phosphate cement liquid molecules have kinetic energy which continuously separates it from the liquid surface. Liquid molecules in the sealed tube are trapped and bump into the tube walls. These bumping particles will return to the liquid surface. This happens continuously with particles separating and returning to the liquid surface. This process causes the tube to become saturated with water gas. At a constant temperature, stability is reached between the liquid and the saturated water gas resulting in a saturated water gas pressure. This phenomena shows that even in a tightly sealed tube, the liquid particles keep evaporating resulting in a saturated water gas pressure [18,19]. When compared visually, the liquid cement component of group III (closest to the expiry date) looked darker than the other groups. This was caused by the evaporation process that separates the water and phosphate acid components causing the liquid cement component to look darker [16].

Cement storage that ignores temperature could affect the evaporation process. For example, while shipping material, including storage during the shipping process, the temperature may not be in accordance with the manufacturer's suggested temperature range. This triggers a slow decrease in the quality of the material. In this research, it was difficult to monitor the material during shipping and storage before the research occurred. Thus, if a dental practitioner buys or uses dental material that is almost expired, they should understand that all dental materials can experience decreased quality or degeneration of its components. Dental practitioners need to judge whether the material's density properties are still good and if the storage temperature was in accordance with the manufacturer's standards, so that the material can still provide the required properties. Moreover, dental materials close to the expiry dates should not be traded anymore because the material properties can decrease, like compressive strength, that can be quite far below ISO standards, as is the case for zinc phosphate cement. Distributors of dental materials also should pay attention to sending, storage, and material distribution which should be in accordance with the manufacturer's guidelines so that the material quality is retained and does not experience decreasing properties. These points are appropriate for Indonesia's tropical climate. If these things are ignored, the shelf life or length of storage time, for some materials, will decrease, and the materials can expire before the manufacturer's expiry date. Zinc phosphate cement that continuously experiences decreasing material properties will not provide suitable compressive strength, or other properties, required for luting or for a restoration base.

4. Conclusion

In this research, it was concluded, that the further zinc phosphate cement is away from its production time and closer to its expiry date, it exhibits decreasing compressive strength. Further research is required about the effect of shelf life on the compressive strength of zinc phosphate cement with the storage temperatures and density of each group determined before the analysis.

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