

# Clinical AND TECHNICAL CONSIDERATIONS OF LUTING AGENTS FOR FIXED PROSTHODONTICS

GUEST EDITORS: CORNELIS H. PAMEIJER, PER-OLOF GLANTZ,  
AND J. ANTHONY VON FRAUNHOFER





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## Editorial

# Clinical and Technical Considerations of Luting Agents for Fixed Prosthodontics

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The selection of an appropriate luting agent for final cementation of fixed restorations is no longer an easy decision. The numerous materials from which restorations can be fabricated demand a thorough knowledge of not only the material(s) they are made of but also knowledge of the properties of luting agents. No longer can zinc phosphate cement be used for all fixed restorations that need cementation, as has been the case since its inception, late 1800s, until the 1970s. With the introduction of new restorative materials and clinical applications such as non-precious alloys, feldspathic veneers, all-ceramic restorations, zirconium, lithium disilicate, the demand for more suitable cements developed somewhat in tandem with new materials and clinical techniques. As a result, today's market is flooded with cements, and more are being introduced on a regular basis. Even for the expert and researcher, the combination of these cements with the large variety of restorative materials would be a daunting task to test, and frequently the clinician has to hope that the choice is the proper one.

This special issue presents a review of luting agents and attempts to bring the practitioner up to date with new developments. Of particular promise in restorative dentistry are the bioactive luting agents that have sealing and remineralizing potential. In this regard, a common misconception is that a luting agent must have high retentive values of its own. The reality is that a luting agent in addition to being an adhesive primarily acts as a seal or gasket to prevent bacteria from penetrating the tooth-restoration interface. Retention is primarily determined by the mechanical resistance and geometry of the preparation.

The authors would like to thank the many reviewers who participated in the evaluation of the twenty submitted manuscripts. Of these, eight manuscripts were accepted and are presented here.

A comprehensive literature review by C. Pameijer highlights composition, physical properties, and clinical applications of luting agents since their inception late 1880s until today with an introduction of the latest developments. A chart with clinical indications is included, which is intended as a guide to selecting an appropriate luting agent. It should be noted that the author pointed out that this chart is strictly based on personal experience and research; much of which has been conducted by the author.

T. Abo and coworkers compared the microtensile bond strengths ( $\mu$ TBSs) of three self-adhesive luting cements and a control (Panavia F 2.0) between ceramics and resin cores and examined their relation to cement thickness of 25, 50, 100, or 200  $\mu$ m. The three self-adhesive cements scored lower  $\mu$ TBSs than the control that required etching and a primer before cementation. A cement thickness of 50 or 100  $\mu$ m tended to induce the highest  $\mu$ TBS, which are clinical parameters that are usually accepted in spite of the recommended 40  $\mu$ m that is advocated by the American Dental Association.

I. Costa Sousa Oliveira and coworkers assessed the effect post-cementation waiting time for core preparation of cemented cast posts and cores had on retention in the root canal. They tested two different luting materials on sixty extracted human canines. The post and cores were fabricated in cast nickelchromium and luted with zinc phosphate (ZP) cement or resin cement. The specimens were divided into

3 groups ( $n = 10$ ) according to the waiting time for core preparation: tested without preparation (control), after 15 minutes and after 1 week after the core cementation. A tensile load test was applied until failure. Significantly higher ( $P < 0.05$ ) tensile strength values were obtained for ZP cement; however, core preparation and postcementation waiting time did not affect the retention strength. The authors concluded that ZP was the best material for intraradicular metal posts cementation. It should be noted, however, that the results do not necessarily apply to all metals that typically are used for post and core fabrication.

In an in vivo study by D. Gemalmaz and co-workers, disintegration of four luting agents was evaluated using a gold intraoral sample holder that had four holes of 1.4 mm diameter and 2 mm depth, which were filled with zinc phosphate (Phosphate Kulzer), a glass ionomer (Ketac Cem), a resin-modified-glass ionomer (Fuji Plus), and a resin cement (Calibra). The holder was soldered onto the buccal surface of an orthodontic band, which was cemented to the first upper molar in 12 patients. Impressions were made at baseline and 6, 12, and 18 months from which epoxy replicas were made, which were scanned with an optical scanner. Total volume loss was calculated. The rank order of mean volume loss was as follows: Phosphate cement > Ketac Cem = Fuji Plus = Calibra. Cement type and time had statistically significant effects on volume loss of cements ( $P < 0.001$ ). Of interest here was the fact that the disintegration of glass ionomer and resin-based cements was not statistically significantly different.

P. Kesrak and C. Leevailoj designed a study to determine the hardness of two light curing resin cements under five different ceramic discs measuring 0.5, 1.0, 1.5, and 2.0 mm in thickness. They concluded that resin cements polymerized under different ceramic materials and thickness showed statistically significant differences in Knoop hardness.

A new hydraulic calcium silicate cement designed for restorative dentistry (Biodentine) was compared with a resin-modified glass ionomer cement (Ionolux) in open-sandwich restorations covered with a light-cured composite by S. Koubi and co-workers. Each group consisted of 5 samples including 5 for the positive and 5 for the negative control. After simultaneously thermocycling and mechano-cycling using a fatigue cycling machine (1,440 cycles, 5–55°C; 86,400 cycles, 50 N/cm<sup>2</sup>), the specimens were then stored in phosphate-buffered saline to simulate aging for 1 year. The samples were then submitted to glucose diffusion. Statistical analysis of the data demonstrated that there was no difference between the Biodentine and the Ionolux group. The calcium silicate-based material performed as well as the resin-modified glass ionomer cement in open-sandwich restorations.

Antibacterial properties are a desirable feature of luting agents. E. Unosson and co-workers designed a clinically relevant laboratory experiment and compared 4 cements (a self-etching cement, a glass ionomer cement, a hybrid calcium aluminate cement, and a zinc phosphate cement) to 2 reference cements (calcium aluminate and glass ionomer cement) and a negative control (PMMA). Antibacterial properties were tested after 10 minutes, 1 and 7 days

using *Streptococcus mutans*. Viable bacteria in direct contact with the samples were determined with a metabolic assay containing resazurin. Furthermore, effect of F and pH was also evaluated. The results indicated that antibacterial properties in descending sequence were calcium aluminate cement > Ceramir Crown & Bridge > and RelyXTM Unicem. KetacTM Cem, Harvard Cement, and the reference glass ionomer cement showed bacteria contents either higher than or not significantly different from the PMMA control. Furthermore pH levels below 6.3 and above 9.0 were found to have negative effects on bacterial proliferation while the more basic the cement was, the stronger the antibacterial properties. These findings may explain tissue health around crown margins of certain cements that have a high pH.

In the J. von Fraunhofer paper, an in-depth discussion on adhesion and cohesion is presented. The text is amply illustrated with detailed drawings that explain the basic principles in a graphic way. Adhesion principles in dentin bonding are also highlighted. It may seem to the reader that the basics that are discussed have no direct bearing on clinical dentistry. The opposite is true. Understanding these principles allows a practitioner to understand success and failure in dentistry much better and can contribute in the selection of an appropriate luting agent.

It is hoped that the information that is provided in this issue will help the practitioner in making prudent decisions that will offer patients a restoration that has a long life span and offers the dentist the assurance that his/her work will last for many years.

Cornelis H. Pameijer  
Per-Olof Glantz  
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## Research Article

# Microtensile Bond Strength of Self-Adhesive Luting Cements to Ceramics

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The purpose of this paper was to compare the bond strengths of the self-adhesive luting cements between ceramics and resin cores and examine their relation to the cement thickness. Three self-adhesive luting cements (Smartcem, Maxcem, and G-CEM) and a resin cement (Panavia F 2.0) for control were used in the paper. The thickness of the cements was controlled in approximately 25, 50, 100, or 200  $\mu\text{m}$ . Each 10 specimens were made according to the manufacturers' instructions and stored in water at 37°C. After 24 hours, microtensile bond strength ( $\mu\text{TBS}$ ) was measured. There were significant differences in cements. Three self-adhesive cements showed significantly lower  $\mu\text{TBS}$ s than control that required both etching and priming before cementation (Tukey,  $P < 0.05$ ). The cement thickness of 50 or 100  $\mu\text{m}$  tended to induce the highest  $\mu\text{TBS}$ s for each self-adhesive luting cements though no difference was found.

## 1. Introduction

Esthetic dentistry, including ceramic restorations, is now a great demand from the patients. CAD/CAM technology in dentistry has also become popular. One of the technologies, CEREC system, since its development in 1985, has improved the software and hardware for easier operation and better adaptation. The current CEREC 3 system can fabricate more precise inlays, onlays, crowns, and veneers. In a review on the CEREC restorations, Fasbinder summarized the postoperative sensitivity, restoration fracture, color match, margin adaptation, clinical longevity, and clinical performance [1]. However, the CAD/CAM system still has a problem with the fitting quality of the restorations. Mörmann and Schug compared the precision of fit between the CEREC 1 and CEREC 2 systems [2]. They reported that the mean marginal interface was  $84 \pm 38 \mu\text{m}$  for CEREC 1-generated inlays and  $56 \pm 27 \mu\text{m}$  for CEREC 2-generated inlays. Nakamura et al. reported a marginal gap of 53 to 67  $\mu\text{m}$  for CEREC 3-generated crowns [3].

Vitablocs Mark II (Vita Zahnfabrik, Germany), conventional feldspathic ceramic, is generally used in the CEREC system. The ceramic restorations are usually cemented with resin-based composite luting agent, after surface treatments necessary for the bonding. In the CEREC restoration, the luting material may be charged of two functions as a luting material and a restorative material to adhere between the tooth substrates and CEREC restoration with good mechanical properties and reliable bond capacity [4]. Therefore, the failure of the luting material at the margin may affect the longevity of restorations. In other words, proper selection of a luting agent is a last important decision in a series of steps that require meticulous execution and will determine the long-term success of fixed restorations [5].

Recently, newly developed resin luting cements called "self-adhesive luting cements" have been commercialized from several manufacturers. These materials feature that the adhesion is possibly achieved to various surfaces without surface pretreatment such as air-abrasion and/or HF-etching.

However, there is little information on the performance of self-adhesive luting cements in the CEREC restorations without surface pretreatment.

*In vitro* bonding efficacy is often evaluated by measuring bond strength as well as morphological structures at the bonding interface. Therefore, the purpose of this study was to compare the bond strengths of the self-adhesive luting cements with different cement thickness, simulating the luting between ceramics and resin abutments without surface pretreatment.

## 2. Material and Methods

**2.1. Specimen Preparation.** Commercial 3 self-adhesive luting cements (Smartcem, Maxcem, and G-CEM) and a control cement (Panavia F 2.0) were used to bond two selected adherends, a ceramic block and resin core in this study (Table 1). Feldspathic ceramic blocks (Vitablocs Mark II; Vita Zahnfabrik, Germany) were horizontally cut with a low-speed diamond saw (Isomet; Buehler, Lake Bluff, IL, USA) and ground with #600 SiC paper to standardize the surface roughness. For preparation of the resin core blocks (Figure 1), core resin (Clearfil DC Core Automix; Kuraray Medical, Tokyo, Japan) was filled into a silicon mold (area:  $8 \times 10 \text{ mm}^2$ ; height: 5 mm) as a bulk. The resin was irradiated from both opposing sides for 40 sec each with Optilux 501 ( $700 \text{ mW/cm}^2$ ; SDS Kerr, Danbury, CT, USA), then post-cured for 5 min within a box of  $\alpha$ -Light (Morita, Tokyo, Japan). The core resin blocks were ground with # 600 SiC paper after 24 h storage at  $37^\circ\text{C}$ .

**2.2. Microtensile Bond Strength ( $\mu\text{TBS}$ ) Test.** The surface of the core resin block was covered with masking tapes (transparent tape with a circular hole, 6 mm in diameters) to standardize cement thickness: 25, 50, 100, and  $200 \mu\text{m}$ . A pilot study confirmed the thickness variation was  $\pm 1 \mu\text{m}$  for each group. Three self-adhesive luting cements were mixed according to the manufacturers' instructions and filled into the hole of the tape without surface treatment (Table 2). Then, a ceramic block was put on it with mild finger pressure. Before cementation with Panavia F 2.0, both adherend blocks were etched with K-etchant Gel (Kuraray Medical, Tokyo, Japan) and silanated with the mixture of Clearfil SE primer (Kuraray Medical, Tokyo, Japan) and Clearfil Porcelain Bond Activator (Kuraray Medical, Tokyo, Japan) according to the manufacturer's instructions (Table 2). The cement was laterally irradiated from 2 opposing sides under each irradiation condition. The specimens were sectioned into  $1.0 \times 1.0 \text{ mm}$  beams ( $n = 10 \times 16$  groups) after 24 h storage in water at  $37^\circ\text{C}$ . Individual beams were then attached to a Ciucchi's device [6] with cyanoacrylate glue (Model Repair II Blue; Dentsply-Sankin, Tochigi, Japan), and  $\mu\text{TBS}$ s were measured using a universal testing machine (EZ Test; Shimadzu, Kyoto, Japan) at a crosshead speed of  $1.0 \text{ mm/min}$  (Figure 2).

**2.3. Failure Analysis.** After measuring  $\mu\text{TBS}$ s, the specimens were examined using Scanning Electron Microscope (SEM; DS-750, Topcon, Japan) to determine the failure modes.

Failure modes were categorized as follows: adhesive failure at the interface between ceramic/core resin and cement, cohesive failure within cement, or mixed failure.

**2.4. Statistical Analyses.** The results of the  $\mu\text{TBS}$  test were analyzed with two-way ANOVA with variables of cements and cement thickness. Multiple comparisons were performed with Tukey's HSD test. The statistical analyses were carried out at 5% level of significance.

## 3. Results

The means and standard deviations (SD) of  $\mu\text{TBS}$ s were given in Table 3. Two-way ANOVA showed an interactive influence between the cements and cement thickness ( $P < 0.05$ ). The multiple comparisons by Tukey's HSD test revealed significant differences between cements ( $P < 0.05$ ).

Panavia F 2.0 gave the stable and higher  $\mu\text{TBS}$ s than the other 3 cements regardless of the cement thicknesses ( $P < 0.05$ ). In 3 self-adhesive luting cements, there was no significant difference in  $\mu\text{TBS}$ s among cement thickness, while the highest  $\mu\text{TBS}$  was to be given between  $50 \mu\text{m}$  (Smartcem and G-CEM) and  $100 \mu\text{m}$  (Maxcem) (Table 3).

SEM analysis revealed that fracture mode was dominantly cohesive failure in the cement regardless of the type of cement and cement thickness.

## 4. Discussion

In this study, adhesion between ceramics and core resin was examined, simulating the luting between CEREC restorations and resin abutments.

Mazzitelli et al. concluded that the predominance of acid-base reactions or radical polymerization might explain the different responses to substrate wetness and raise concerns regarding their universal application both on vital and pulpless teeth [7]. Also,  $\mu\text{TBS}$ s is commonly affected by the properties of the adherends. Therefore,  $\mu\text{TBS}$ s in this study were measured using uniform substrates as fundamental indexes to reduce the individual difference of the adherends. Also, the cement line was irradiated from 2 opposing sides after the cementation of two kinds of blocks because several self-etching resin cements were to be used in the dual-cure mode under optimal polymerization condition [8].

Ceramic surface is usually sandblasted or abraded with diamond bar, and/or etched (e.g., phosphoric acid or hydrofluoric acid) prior to silane treatment [9, 10]. However, for Panavia F 2.0, etching and priming were required before cementation, but hydrofluoric acid etching not always necessary for ceramics surface. In a usual clinical way, the pretreatment with phosphoric acid and saline-coupling agent before cementation is simple and effective [11]. Besides, newly developed self-adhesive luting cements are featured on the reducible treatment. Actually, one-step approach with self-adhesive luting cements seemed to be simpler and less technique-sensitive than the conventional resin cements. This study focused on the effect of cement thickness on the bond between core resins and ceramic surface. The bond strength is attributed to a lot of variables involved. The reduced factors might facilitate to understand the bond

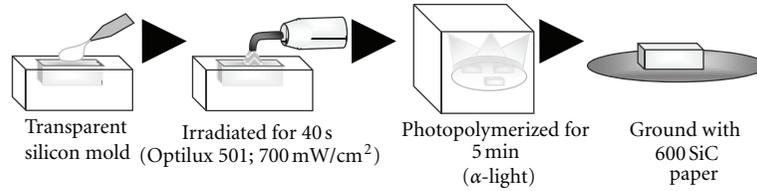


FIGURE 1: Schematic illustration of the procedure for core resin preparation.

TABLE 1: Composition of the commercial resin-based composite luting cement.

Product name (Shade)	Lot no.	Composition	Manufacturer
Smartcem (Natural)	R0707B1	Base Paste: HEMA, 4-MET, PEM-F, Initiator, Inhibitor, others Catalyst Paste: 1,3-Butanediol dimethacrylate, Sulfuric acid salt, Tertiary amine, Inhibitor, others	DENTSPLY-Sankin, Tochigi, Japan
Maxcem (Clear)	2855305	Base Paste: UDMA, Camphorquinone, Fluoroaluminosilicate glass, others Catalyst Paste: Bis-GMA, TEGDMA, Glycerophosphatedimethacrylate, Barium aluminoborosilicate glass, others	SDS Kerr, Orange, USA
G-CEM (A2)	0702061	Powder: Fluoroaluminosilicate glass, Initiator, Pigment Liquid: 4-MET, Phosphoric acid ester monomer, UDMA, Dimethacrylate, water, Silicon dioxide, Initiator, Inhibitor	GC, Tokyo, Japan
Panavia F 2.0 Paste (Brown)	0293AB, 0155AA	Paste A: MDP, Methacrylate monomer, Filler, Initiator Paste B: Methacrylate monomer, Filler, NaF, Initiator, Pigment	Kuraray Medical, Tokyo, Japan

HEMA: 2-hydroxyethyl methacrylate; 4-MET: 4-methacryloxyethyl trimellitate; PEM-F: 5-methacryloxyethylcylophosphazene monofluoride; UDMA: urethane dimethacrylate; Bis-GMA: bisphenol-A-glycidyl dimethacrylate; TEGDMA: triethyleneglycol dimethacrylate; MDP: 10-methacryloyloxydecyl dihydrogen phosphate.

Before cementation with Panavia F 2.0, specimens were etched with K-etchant and silanated with Clearfil SE primer and Porcelain Bond Activator.

TABLE 2: The procedures for each resin-based composite luting cement.

Smartcem	Maxcem	G-CEM	Panavia F 2.0
↓	↓	↓	↓
hand-mixed for 20 sec	auto-mixed	hand-mixed for 20 sec	( etched for 5 sec rinsed and dried silanated for 5 sec )
↓	↓	↓	↓
cemented and held for 2 min	cemented and held for 90 sec	cemented and held for 90 sec	hand-mixed for 20 sec
↓	↓	↓	↓
irradiated for 30 sec	irradiated for 20 sec	irradiated for 10 sec	cemented and held for 2 min
			↓
			irradiated for 20 sec

TABLE 3: Microtensile bond strength (MPa).

	Smartcem	Maxcem	G-CEM	Panavia F 2.0
25 μm	15.38 (4.06) <sup>a,b,c,d</sup>	13.75 (5.91) <sup>a,b,c,d</sup>	12.53 (8.68) <sup>a,b,c</sup>	45.32 (8.72) <sup>e</sup>
50 μm	17.85 (5.64) <sup>b,c,d</sup>	16.38 (6.17) <sup>a,b,c,d</sup>	22.60 (6.40) <sup>d</sup>	46.35 (7.76) <sup>e</sup>
100 μm	9.55 (2.38) <sup>a,b</sup>	20.16 (1.90) <sup>c,d</sup>	16.98 (3.53) <sup>a,b,c,d</sup>	43.72 (6.16) <sup>e</sup>
200 μm	8.70 (2.63) <sup>a</sup>	16.41 (3.88) <sup>a,b,c,d</sup>	13.72 (2.74) <sup>a,b,c,d</sup>	39.39 (9.21) <sup>e</sup>

Mean (SD). Same letters denote no significant difference ( $P > 0.05$ ).

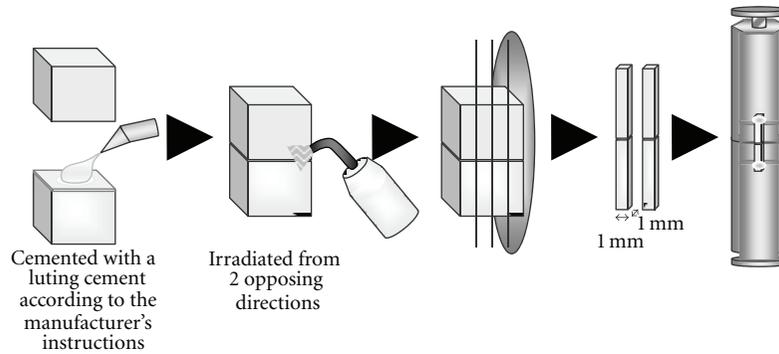


FIGURE 2: Schematic illustration of the procedure for  $\mu$ TBS measurement.

performance. Thus, the pretreatment with hydrofluoric acid was not carried out in this study. The further study would make clear the effect of surface pretreatment such as a hydrofluoric acid etching. Kamada et al. reported the dual-cured resin luting agents provided much higher early bond strength to ceramic blocks for CEREC than chemically cured resin luting agents and maintained durable bond strength even after 20,000 thermocycles [12]. In this study, all 4 materials were dual-cure luting cements. Three self-adhesive luting cements showed relatively lower  $\mu$ TBSs than the control material, Panavia F 2.0. The surface pretreatment might be one of the reasons for the different bond performance between self-adhesive luting cements and control, Panavia F.

All self-adhesive luting cement used in the study contains phosphoric ester monomer. Besides, 4-MET is added in both Smartcem and G-CEM. These functional acidic monomers possibly contribute to the adhesion. Further, The dominant fracture mode, that is, cohesive failure within the cement regardless of the brand of the cements, indicates that tensile stress concentrated to the cement body rather than the bonding interfaces. This implies that the mechanical property of the resin matrix mainly contributes to the bonding performance of the cements.

Han et al. reported that the pH values of 3 self-adhesive luting cements, Smartcem, Maxcem, and G-CEM, were lower than 4 at 90 seconds after mixing; G-CEM was the lowest (pH 1.8) and Smartcem was the highest (pH 3.6) [13]. They also stated that the low pH might have an etching effect but an adverse influence on the adhesion if the low pH were left too long. Several self-etch cements tend to show high initial acidity and gradual rise of pH during setting [8]. In this study, Smartcem showed relatively lower  $\mu$ TBSs than the others, and G-CEM showed slightly higher  $\mu$ TBSs than Smartcem. These differences may be due to the etching effect by the different pH.

The results of the study also suggested that the thickness of cements affected the  $\mu$ TBSs for all self-adhesive luting cement. Filler size and consistency of the luting composites affect the film thickness [14, 15]. Filler particle size in all 3 self-adhesive cements was less than 5  $\mu$ m. Two cements except Smartcem contain angular-shaped inorganic fillers [13]. The filler shape of Smartcem may be a powerful variable

for the cement thickness though its diffusion in the resin matrix.

G-CEM contains UDMA as a cross-linking monomer, owing to a lower molecular weight and to the greater flexibility of the urethane linkage [16]. Maxcem is mainly composed of base monomers, UDMA, Bis-GMA, and TEGDMA. Asmussen and Peutzfeldt reported that varying the relative amounts of UDMA, Bis-GMA, and TEGDMA had a significant effect on the mechanical properties of the resin composition [16]. Therefore, it can be speculated that base monomers have a large influence on the  $\mu$ TBSs of the different cement thicknesses. Moreover, the ratio of base monomers and functional acidic monomers could be associated with the mechanical properties of the cement.

Usually, there is a relatively large discrepancy between a CEREC restoration and cavity walls due to the accuracy of the optical impression and milling. The space must be filled with luting cement. Therefore, the varied bond strength by the cement thickness could be disadvantageous for the longevity of the restoration.

Further study should be carried out to investigate the between mechanical properties of the self-adhesive luting cements and their bonding capacity, and also longevity of the bonding.

## 5. Conclusion

Three self-adhesive luting cements showed lower  $\mu$ TBSs than Panavia F 2.0 that required surface treatments for the bonding. There were significant differences between cements; Smartcem showed the lowest and Panavia F 2.0 the highest  $\mu$ TBSs (Tukey's HSD,  $P < 0.05$ ). Panavia F 2.0 gave the stable  $\mu$ TBSs regardless of the cement thickness. The results suggested that the cement thickness might have an influence on  $\mu$ TBSs, for the self-adhesive luting cements.

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## Research Article

# Surface Hardness of Resin Cement Polymerized under Different Ceramic Materials

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**Objectives.** To evaluate the surface hardness of two light-cured resin cements polymerized under different ceramic discs. **Methods.** 40 experimental groups of 2 light-cured resin cement specimens (Variolink Veneer and NX3) were prepared and polymerized under 5 different ceramic discs (IPS e.max Press HT, LT, MO, HO, and Cercon) of 4 thicknesses (0.5, 1.0, 1.5, and 2.0 mm). Those directly activated of both resin cements were used as control. After light activation and 37°C storage in an incubator, Knoop hardness measurements were obtained at the bottom. The data were analyzed with three-way ANOVA, *t*-test, and one-way ANOVA. **Results.** The KHN of NX3 was of significantly higher than that of Variolink Veneer ( $P < 0.05$ ). The KHN of resin cement polymerized under different ceramic types and thicknesses was significant difference ( $P < 0.05$ ). **Conclusion.** Resin cements polymerized under different ceramic materials and thicknesses showed statistically significant differences in KHN.

## 1. Introduction

Currently, there is an increased demand for esthetic restorations, especially all-ceramic restorations, including all-ceramic crowns, inlays, onlays, and veneers. Therefore, many new ceramic systems have been developed. Current ceramic materials have numerous superior properties, such as their esthetic lifelike appearance, biocompatibility, chemical stability, and high compressive strength. Continuing development in ceramic core materials has made all-ceramic restorations a more valuable clinical option. Ceramic core materials are categorized into 3 different types: glass, alumina based, and zirconia [1].

In addition to the physical properties of ceramics, luting materials are important for the longevity of ceramic restorations. The use of resin cement in combination with a dental adhesive will strengthen all-ceramic restorations and influence the longevity of the restoration [2]. Furthermore, resin cement has an effect on the esthetics of restorations due to the color of the cement. Because ceramic is a translucent material, using tooth-colored resin cement under ceramic

restorations allows the observation of the color of the cement and improves the esthetics of the restoration. Alternatively, some resin cements can obscure dark-colored teeth and that may affect the color of restoration.

Resin cements are composed of methacrylate or Bis-GMA, similar to resin composite. According to the activation mode, resin cements are usually divided into three groups: chemically activated (self-cured), photoactivated (light-cured), and dual-cured, in which the polymerization was affected by both chemical and light activation [3]. Light-cured resin cements use a photoinitiator, primarily camphorquinone; the polymerization process begins when activated by light from the light-curing unit. Light-cured resin cements are often preferred to chemical-cured and dual-cured resin cements because of their on-demand polymerization characteristic. Moreover, this type of resin cement allows for easier manipulation due to the lack of preparation process, such as mixing before use, which results in decreased air incorporation into the cement and also decreased color instability. However, light-cured resin cements also have a limitation associated with the polymerization process as they

require sufficient light to initiate and maintain polymerization, especially in deep cavities or thick restorations that may attenuate the light from the light-curing unit. Incomplete polymerization of materials will affect both physical and biological properties, such as surface hardness, color instability, toxicity from residual monomer [4–7], and decreased bond strength between tooth and restoration (which can also decrease the longevity of the restoration).

The effectiveness of light to initiate polymerization of resin-based materials requires the appropriate wavelength determined by the type of photoinitiator incorporated in the resin-based material [8]. Camphorquinone is effectively activated by light at a wavelength range of 375–500 nm, with a peak maximum absorption at 468–470 nm [9, 10] and also with a light intensity high enough to activate polymerization. Factors affecting light efficiency include the light-curing unit, exposure time, and any object between the light tip and the resin cement [11–13]. Recently, the light emitting diode (LED) light-curing units have become very popular among dental practitioners because of advantages over existing light-curing units. The LED produces a narrow spectrum of light that falls within the absorption spectrum of the camphorquinone [14]. Furthermore, an LED has a lower power requirement and is powered by a rechargeable battery which makes the device a cordless, portable, and lightweight unit with a longer lifespan.

Surface hardness testing is one aspect of the polymerization measurement method [15–17]. It provides a strong correlation to the light intensity used in polymerization activation [18–20]. Hence, this study aimed to evaluate the surface hardness of two light-cured resin cements polymerized under different types and thicknesses of ceramic discs.

## 2. Materials and Methods

For IPS e.max Press (Ivoclar Vivadent, Liechtenstein) ceramic groups, the ceramic discs were fabricated from IPS e.max Press high-translucency ingot (HT-A1), low-translucency ingot (LT-A1), medium-opacity ingot (MO-0), and high-opacity ingot (HO-0), with a 10 mm diameter and thicknesses of 0.5, 1.0, 1.5, and 2.0 mm. The wax patterns, 10 mm in diameter with a level of thickness exceeding 0.2 mm each, were fabricated to the ceramic discs by the lost wax, heat press process. The ceramic discs were polished with an automatic polishing machine (DPS 3200, IMPTECH, South Africa) and silicon carbide paper nos. 400, 600, 800, and 1200, respectively. The final thickness was measured by a digital micrometer (Mitutoyo, Japan).

For Cercon (DeguDent, Germany) ceramic groups, the ceramic discs were fabricated from a Cercon base (white) to a 10 mm diameter and thicknesses of 0.5, 1.0, 1.5, and 2.0 mm. The Cercon base was cut into the framework in a circular shape and trimmed by the silicon carbide paper. The framework required a 30% greater diameter and thickness to compensate for shrinkage during the sintering process. After sintering, the ceramic discs were polished and measured, as previously described.

The resin cements used in this study were Variolink Veneer (Ivoclar Vivadent, Liechtenstein) shade high value +3 and NX3 Nexus Third Generation (Kerr Corporation, USA) shade white opaque. The resin cement was inserted into a black PVC mold with a centered hole 6.0 mm in diameter and 0.5 mm deep. A glass slab (0.04 mm thick) was placed above the mold and resin cement. The resin cement underwent light activation in two modes: direct light activation (control) or light activation through ceramic discs (experimental), with 5 ceramic groups and 4 thicknesses each. In the experimental groups, the ceramic discs were placed between the tip of the light guide of the light-curing unit and the glass slab covering the resin cement before activation. The resin cement was light activated by an LED light-curing unit (Demi, Kerr Corporation, USA) with an irradiance of 1,450 mW/cm<sup>2</sup> for 40 seconds, in contact with the ceramic material or glass slab. The intensity of the light-curing units was measured with a hand-held radiometer (L.E.D. radiometer by Demitron, Kerr Corporation, USA) that was recalibrated after 10 times of usage. The specimens were stored in an incubator (CONTHERM 160 M, CONTHERM Scientific Ltd., New Zealand) at 37°C for approximately 24 hours. Forty two groups of 12 resin cement specimens each were tested.

The micro-hardness tester (FM-700e TYPE D, FUTURETECH, Japan) with 50-gram force for 15 seconds was used for Knoop hardness testing. Three indentations were made on the bottom surface of each specimen, with a 1 mm distance between indentations, and the means were then calculated. Measurements were made under 40x magnification.

*Statistical Analysis.* SPSS software version 17 was used to analyze the results at a 0.05 significance level ( $P < 0.05$ ). The effects of resin cement types, ceramic types, and thicknesses of ceramic on resin cement hardness were analyzed using three-way ANOVA. The independent *t*-test was used to compare the 2 different types of resin cement. To compare the surface hardness of light-curing resin cement cured through different thicknesses of ceramics, we used one-way ANOVA and Tukey's multiple comparison test. Finally, the one-way ANOVA and Tukey's multiple comparison test were used to compare the differences of the resin cement surface hardness cured through different types of ceramic having the same thickness.

## 3. Results

Table 1 shows the surface hardness value of two resin cements when polymerized under different types and thicknesses of ceramic discs. The surface hardness of Variolink Veneer was statistically lower than that of NX3 in all experimental groups. The surface hardness of both resin cements (Variolink Veneer and NX3) when polymerized under ceramic discs presented statistically significant differences from the control. For Variolink Veneer, the surface hardness of resin cement polymerized under IPS e.max Press HT 2.0 mm, LT 2.0 mm, MO 1.5, 2.0 mm, HO 1.0, 1.5, and, 2.0 mm and Cercon 1.0, 1.5, and 2.0 mm was significantly lower than that

TABLE 1: The mean (KHN)  $\pm$  standard deviation of surface hardness of two resin cements when polymerized under different ceramic a.

Ceramic/thickness (mm)	KHN (mean $\pm$ SD)	
	Variolink Veneer	NX3
Control	21.64 $\pm$ 3.7 <sup>1</sup>	30.28 $\pm$ 1.8 <sup>2</sup>
e.max HT/0.5	19.39 $\pm$ 3.8 <sup>1Aa</sup>	30.16 $\pm$ 1.8 <sup>2Ne</sup>
e.max HT/1.0	18.39 $\pm$ 3.3 <sup>1ABb</sup>	29.80 $\pm$ 2.2 <sup>2Nf</sup>
e.max HT/1.5	17.16 $\pm$ 2.9 <sup>1ABc</sup>	27.79 $\pm$ 1.9 <sup>2Nh</sup>
e.max HT/2.0	15.38 $\pm$ 2.1 <sup>1Bd*</sup>	24.83 $\pm$ 3.3 <sup>2Ok*</sup>
e.max LT/0.5	19.42 $\pm$ 3.2 <sup>1Ca</sup>	28.30 $\pm$ 2.3 <sup>2Pe</sup>
e.max LT/1.0	18.40 $\pm$ 3.1 <sup>1CDb</sup>	27.29 $\pm$ 2.3 <sup>2POfg</sup>
e.max LT/1.5	16.45 $\pm$ 3.2 <sup>1CDc</sup>	26.90 $\pm$ 2.1 <sup>2QRhi*</sup>
e.max LT/2.0	15.30 $\pm$ 3.2 <sup>1Dd*</sup>	22.99 $\pm$ 2.1 <sup>2Rk*</sup>
e.max MO/0.5	19.43 $\pm$ 3.2 <sup>1Ea</sup>	28.46 $\pm$ 1.5 <sup>2Se</sup>
e.max MO/1.0	17.97 $\pm$ 3.2 <sup>1EFb</sup>	27.45 $\pm$ 2.2 <sup>2Sfg</sup>
e.max MO/1.5	16.47 $\pm$ 3.3 <sup>1EFc</sup>	26.31 $\pm$ 1.8 <sup>2Shi*</sup>
e.max MO/2.0	14.81 $\pm$ 2.8 <sup>1Fd*</sup>	23.81 $\pm$ 2.4 <sup>2Tkm*</sup>
e.max HO/0.5	19.81 $\pm$ 3.9 <sup>1Ga</sup>	29.48 $\pm$ 2.6 <sup>2Ue</sup>
e.max HO/1.0	18.15 $\pm$ 3.4 <sup>1GHb</sup>	27.16 $\pm$ 2.4 <sup>2UVfg*</sup>
e.max HO/1.5	16.34 $\pm$ 2.8 <sup>1HJc*</sup>	25.51 $\pm$ 2.3 <sup>2Vhi*</sup>
e.max HO/2.0	13.01 $\pm$ 2.1 <sup>1Jd*</sup>	20.08 $\pm$ 2.6 <sup>2Wkm*</sup>
Cercon/0.5	17.66 $\pm$ 3.3 <sup>1Ka</sup>	28.80 $\pm$ 2.3 <sup>2Xe</sup>
Cercon/1.0	16.73 $\pm$ 2.8 <sup>1KLb*</sup>	27.11 $\pm$ 2.5 <sup>2XYg*</sup>
Cercon/1.5	14.47 $\pm$ 2.4 <sup>1LMc*</sup>	24.70 $\pm$ 2.7 <sup>2Yj*</sup>
Cercon/2.0	13.15 $\pm$ 3.1 <sup>1Md*</sup>	21.82 $\pm$ 2.4 <sup>2Zm*</sup>

Different numbers in the same row indicate significant difference ( $P < 0.05$ ) between 2 resin cements. Different uppercase letters in the same column indicate significant difference ( $P < 0.05$ ) among ceramic thicknesses in each ceramic type.

Different lowercase letters in the same column indicate significant difference ( $P < 0.05$ ) among ceramic types in each ceramic thickness.

\*Indicates significant difference ( $P < 0.05$ ) from control group.

of the control group. The surface hardness of NX3, polymerized under IPS e.max Press HT 2.0 mm, LT and MO at a thickness level of 1.5, 2.0 mm, and HO and Cercon at a thickness level of 1.0, 1.5, and 2.0 mm was significantly lower than that of control. Furthermore, the surface hardness of both resin cements when polymerized under each ceramic type showed statistically significant differences between thicknesses. Resin cement polymerized under 2.0 mm ceramic discs tended to have the lowest surface hardness value in each ceramic.

When comparing the surface hardness value of two resin cements polymerized under different ceramic types with the same thickness, the surface hardness of Variolink Veneer in all thicknesses of ceramic showed no statistically significant differences among all ceramic types. The resin cement polymerized under IPS e.max Press HT and Cercon tended to have the highest and lowest surface hardness, respectively, through each thickness range. For NX3, the surface hardness of cement polymerized under 0.5 mm ceramic discs showed no statistically significant differences among all ceramic types. When NX3 was polymerized under 1.0, 1.5, and 2.0 mm ceramic discs, the surface hardness of resin cement under IPS e.max Press HT was significantly higher than Cercon. However, when NX3 polymerized under 2.0 mm ceramic discs,

the surface hardness of resin cement under both IPS e.max Press HT and MO was higher than Cercon.

#### 4. Discussion

The use of resin cement for luting restorations, especially all ceramic restorations, is quite common. Adequate polymerization of resin cement will result in high-bond strength between tooth and restoration. Light intensity is one of the most important factors that affects polymerization of light-cured resin cements. Recent studies have shown a positive correlation between light intensity and the degree of conversion of restorative materials [21–23]. Rueggeberg et al. [12] suggested that the adequate intensity for a light-curing unit is 400 mW/cm<sup>2</sup> in order to initiate polymerization of resin-based material, but is unsuitable when the light-curing unit irradiated light with intensity under 233 mW/cm<sup>2</sup>. The ISO [24] also suggested a minimum intensity of 300 mW/cm<sup>2</sup> in the 400–515 nm wavelength bandwidth. The LED light-curing unit used in this study provided light intensity up to 1,450 mW/cm<sup>2</sup>, as measured by a radiometer, and induced a high degree of polymerization and surface hardness of resin cements. However, when irradiating through ceramic discs,

the light intensity decreased as a function of the type and thickness of the ceramics [25–27].

The dental ceramics used in this study were IPS e.max Press and Cercon, which are indicated for veneer and crown fabrication. The IPS e.max Press, a lithium disilicate glass ceramic, has 4 types corresponding to opacity: high translucency (HT), low translucency (LT), medium opacity (MO), and high opacity (HO). Cercon is one of the CAD/CAM zirconia ceramics possessing high strength and opacity [1]. In this study, when irradiating light through Cercon and IPS e.max Press, the light intensity through Cercon was lower compared with IPS e.max Press, which has lower opacity.

Surface hardness is one of the most effective methods to evaluate the polymerization of resin cement. Many studies have shown that Knoop hardness has a positive correlation with the degree of conversion of resin cement [15, 17]. Furthermore, Knoop hardness has also been reported to be related to the light intensity of the light-curing unit [20, 27]. Resin cement which received higher light intensity had better polymerization and higher Knoop hardness than that receiving lower light intensity. In this study, surface hardness was measured at the bottom surface of specimens, opposite to the light activation surface, to show the degree of polymerization of the whole material. A study by Aguiar et al. [28] has shown the surface hardness of the top surface was the highest. It decreased significantly moving from the top toward the bottom of the specimen due to greater distance from the light guide. Moreover, resin cement can disperse light from the light-curing unit as resin matrix and filler particle scatter the light and thus reduce light intensity when passing through resin cement [13, 29]. Consequently, the surface hardness of the top surface does not indicate the hardness of other portions or degree of conversion of materials.

Resin cement polymerized under ceramic discs received lower light intensity as the thicknesses and opacity of ceramic increased. The decrease of surface hardness was statistically significant as a function of change in those parameters [30]. This study found that direct activation resin cement had higher surface hardness than resin cement which was activated through ceramic, especially Variolink Veneer polymerized under Cercon 1.0, 1.5, and 2.0 mm. While both resin cements were polymerized under all ceramic types of 0.5 and 1.0 mm thickness, the surface hardness did not vary from the surface hardness of the control group except NX3 polymerized under IPS e.max Press HO 1.0 mm and Variolink Veneer polymerized under Cercon 1.0 mm. For ceramic thicknesses of 1.5 and 2.0 mm, the surface hardness was different from that of the control group where resin cement was polymerized under ceramic with higher opacity, such as IPS e.max Press HO and Cercon. This may imply that the thickness of ceramic has less effect on high-translucency ceramics than low-translucency or high-opacity ceramics. The surface hardness of resin cements polymerized under high-opacity ceramic was lower than those polymerized under lower-opacity ceramic. The surface hardness of both resin cements polymerized under Cercon zirconia ceramic showed the lowest hardness, while resin cement polymerized under IPS e.max Press HT, a glass ceramic, tended to have the highest hardness of all thicknesses. These results are in line

with the finding of Borges et al. [31] who reported that resin cement polymerized under alumina and zirconia ceramic had lower hardness than cement polymerized under glass ceramic. Furthermore, the study found that NX3 had higher hardness than Variolink Veneer in all groups. These results are likely due to different compositions of resin cement such as types, quantities, and size of filler, which affect polymerization of materials [32, 33].

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## Research Article

# Antibacterial Properties of Dental Luting Agents: Potential to Hinder the Development of Secondary Caries

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A modified direct contact test was used to evaluate the antibacterial properties of four commercially available dental luting agents (RelyX Unicem, Ketac Cem, Ceramir Crown & Bridge and Harvard Cement) and two reference materials (glass-ionomer cement and calcium aluminate cement) compared to a negative-control material (PMMA). *Streptococcus mutans* bacteria were placed in direct contact with specimens that had been aged for 10 min, 1 day, and 7 days, in order to test the antibacterial properties of the materials. A metabolic assay containing resazurin was used to quantify the amount of viable bacteria remaining after the direct contact tests. The effects of pH and fluoride on bacteria proliferation were also evaluated. Strongest antibacterial properties were found for calcium aluminate cement, followed by Ceramir Crown & Bridge and RelyX Unicem. Ketac Cem, Harvard Cement, and the reference glass-ionomer cement showed bacteria content either higher than or not significantly different from the PMMA control in all instances. pH levels below 6.3 and above 9.0 were found to have negative effects on bacterial proliferation. No correlation between either acidic materials or fluoride release and antibacterial properties could be seen; rather, basic materials showed stronger antibacterial properties.

## 1. Introduction

Prosthetic dentistry revolves around the restoration or replacement of lost or missing teeth using crowns, bridges, and other dentures. In fixed partial dentures (FPDs), dental luting agents serve as the link between the prepared, supporting tooth, and the prosthetic tooth material. An ideal dental cement to be used as a luting agent should be biocompatible, inhibit caries or plaque formation, have low solubility, have correct film thickness and viscosity, have long working time and short setting time, have high strength and stiffness comparable to dentin, show no microleakage, permit easy removal of excess material, and exhibit high retention [1]. A wide range of luting agents with varying chemistries and properties are available on the market and strive to meet these high requirements. However, FPDs are prone to failure, with the number one cause of failure being secondary dental

caries [2, 3]. Secondary caries is readily formed in restoration margins or gaps where plaque, a biofilm containing various bacteria, can adhere [4]. Among the bacterial species present in these biofilms, *Streptococcus mutans* is recognized as the one most frequently involved in caries formation [5]. These bacteria produce acids when metabolizing fermentable carbohydrates, which can then dissolve the calcium phosphate mineral content in enamel and dentin, eventually leading to a cavity or failure of the FPD [6]. Colonization of bacteria often occurs at secluded locations in shortage of oxygen and mechanical disturbance and consequently bactericidal properties of dental cements are of particular importance since it is one of the few means by which bacteria can be inhibited in these sites.

Antibacterial properties of dental cements have been evaluated in the past [7–9], and the bactericidal effects are often attributed to their low pH and/or release of fluoride

ions. There is, however, conflicting data as to whether the low-level fluoride release or acidity of currently used materials is sufficient for long-term bactericidal effect, and which class of cement performs the best [7, 9–11].

Two popular assays used to evaluate antibacterial properties of dental cements are the agar diffusion test (ADT) and direct contact test (DCT). While the ADT has been used successfully [7, 12], it has certain limitations. Results are semiquantitative and depend on solubility and diffusion properties of both the material tested and the medium used. To avoid the limitations of ADT, DCT was developed by Weiss et al. [13] and further used in several other studies of similar character [8, 9, 14, 15]. In DCT, outgrowth of bacteria after close contact with a nonsoluble material is quantified by continuous measurements of optical density (OD), which is proportional to the concentration of bacteria present in solution.

In this study, a modified DCT was used to evaluate the antibacterial properties of four commercially available dental cements (three acid-base reacting and one self-etching) and two acid-base reacting reference materials. A metabolic assay containing resazurin was used to quantify the bacteria present in solution after direct contact with the cements. Resazurin is a common metabolic activity indicator that has been shown to be effective in assessing bacterial viability [16] and in biofilm quantification [17]. It is a water-soluble dye that can be reduced to highly fluorescent resorufin by metabolically active bacteria. In addition, the effects of pH and fluoride on bacteria proliferation were evaluated by means of OD measurements.

## 2. Materials and Methods

**2.1. Sample Preparation.** Compositions, powder to liquid (P/L) ratio and suppliers of the dental cements investigated in this study are shown in Table 1. Commercially available products were all prepared in accordance with the manufacturers instructions. RelyX Unicem (RelyX) and Ketac Cem (Ketac) were prepared using the Aplicap Activator and Applier and mixed using a CapMix universal mixing unit (3 M ESPE). Harvard Cement (zinc phosphate, ZP), Ceramir Crown & Bridge (Ceramir), calcium aluminate cement (CA), and glass-ionomer cement (GIC) were all mixed by hand using a stainless steel spatula on a clean surface. After preparation, the cements were transferred to rubber molds, 1.5 mm deep and 5 mm in diameter. Light curing was used for RelyX, while the remaining cements were allowed to set for 7–10 min at 37°C in 100% relative humidity. After setting, samples were removed from the molds and returned to the oven for aging at 37°C in 100% relative humidity for 10 min, 1 day, or 7 days before testing for antibacterial effect. As a control, samples of poly(methyl methacrylate) (PMMA), a biomaterial considered inert in its fully polymerized state, were cut in the same dimensions from a solid rod.

**2.2. Bacterial Strain and Growth Conditions.** *Streptococcus mutans* (strain NCTC 10449) was used to determine growth inhibition activity of the investigated cements, the effects of varying pH, and the bactericidal effect of fluoride. *S.*

*mutans* has frequently been used to test antimicrobial activity [12, 18–21] and is considered a primary etiological agent of caries [5]. *S. mutans* was inoculated in brain-heart infusion (BHI) broth (Sigma-Aldrich, Steinheim, Germany) and cultured anaerobically at 37°C to exponential phase ( $OD_{600} = 1.0$ ). The culture was centrifuged at 4000 rpm for 5 min and the bacteria pellet was resuspended in sterile H<sub>2</sub>O. The concentration of bacteria was adjusted to  $OD_{600} = 1.0$ , which corresponds to  $10^9$  cfu/mL.

**2.3. Direct Contact Test.** The direct contact test (DCT) performed by Weiss et al. [13] is based on turbidimetric determination of continuous bacterial outgrowth from the material under investigation. In the modified direct contact test performed in the current study, resazurin was used as metabolic activity indicator to quantify viable bacteria instead of OD measurements. In the resazurin assay, blue, nonfluorescent resazurin is reduced by metabolic intermediates (e.g., NADPH) to pink resorufin, which is fluorescent and therefore a sensitive indicator of the amount of viable bacteria in the assay [16].

Six samples of each cement type and a control group of six PMMA samples were tested for each aging time. Each sample was placed at the bottom of a well of a 96-well plate (sterile, transparent, flat bottom, CELLSTAR, Greiner Bio-One GmbH, Germany) and 5  $\mu$ L of the *S. mutans* suspension was added and evenly distributed on the sample surface. Samples were then incubated at 37°C for 1 h, during which time the suspension liquid evaporated, ensuring direct contact between bacteria and testing material. Immediately following this step, 135  $\mu$ L of Mueller Hinton (MH) broth culture medium (Fluka) and 15  $\mu$ L resazurin (1.25  $\mu$ g/mL) were added to each well and incubation was continued at 37°C for 100 min, after which fluorescence measurements of each well were made using a multimode microplate reader (Infinite 200 PRO, TECAN, Männedorf, Switzerland) set to 530 nm excitation and 590 nm emission wavelengths [22]. Samples were removed from the wells prior to fluorescence measurement since the testing materials themselves may influence the measurements.

In order to calibrate results from the sample viability assays, a standard curve was made from a set of resazurin assays containing a serial dilution of bacteria. The standard curve provides a quantitative measure of viable bacteria in the sample assays by comparing the fluorescent signals from the sample assays to that of the serial dilution.

**2.4. Antibacterial Effects of pH.** For measuring the effects of varying pH on bacterial proliferation, 10 different buffer solutions (Sigma-Aldrich) ranging from pH 1 to 11 were used. Test solutions comprised of a suspension of *S. mutans* in BHI broth and pH buffer were prepared as detailed in Table 2. A solution containing sterile deionized H<sub>2</sub>O (hereafter referred to as H<sub>2</sub>O) instead of pH buffer was used as control. The pH of H<sub>2</sub>O is around 7 and is not expected to have negative effect on bacterial growth. The resulting pH of the control and test solutions was measured using a pH meter (HI 83141, Hanna instruments). Solutions were then incubated at 37°C and OD measurements at

TABLE 1: Contents, type, supplier, P/L ratio, and possibility of fluoride release of the dental cements investigated.

	Powder	Liquid	Type	Supplier	P/L ratio	Fluoride release
RelyX Unicem	Glass powder, initiator, silica, substituted pyrimidine, calcium hydroxide, peroxy compound, pigment	Methacrylated phosphoric ester, dimethacrylate, acetate, stabilizer, initiator	Resin cement, self-etching	3 M ESPE (Seefeld, Germany)	In capsules	Yes
Ketac Cem Aplicap	Glass powder, pigments	Polycarboxylic acid, tartaric acid, water, conservation agents	Glass ionomer, acid-base reacting	3 M ESPE (Seefeld, Germany)	In capsules	Yes
Harvard zinc phosphate cement	Zinc oxide, magnesium oxide	o-phosphoric acid	Zinc phosphate, acid-base reacting	Harvard Dental International GmbH (Hoppegarten, Germany)	3/2	No
Ceramir Crown & Bridge	Calcium aluminate, strontium fluoride, polyacrylic acid, tartaric acid, strontium aluminofluoride glass	Water, accelerators	Bioceramic, acid-base reacting	Doxa AB (Uppsala, Sweden)	3.2/1	Yes
Calcium aluminate cement reference material	Calcium aluminate	Water, accelerators	Bioceramic, acid-base reacting	Doxa AB (Uppsala, Sweden)	2.5/1	No
Glass ionomer cement reference material	Poly acrylic acid, tartaric acid, strontium aluminofluoride glass, strontium fluoride	Water	Glass ionomer, acid-base reacting	Doxa AB (Uppsala, Sweden)	3.2/1	Yes

TABLE 2: Contents of the reference, control, and test solutions for measuring bactericidal effects of varying pH.

Solution	Contents (mL)			<i>S. mutans</i> (OD <sub>600</sub> = 1.0)
	BHI broth	pH buffer	H <sub>2</sub> O	
Reference	4	—	6	—
Control	3.4	—	6	0.6
Test solutions	3.4	6	—	0.6

600 nm were made on 3 mL aliquots from each solution using a spectrophotometer (UV-1650, Shimadzu, Kyoto, Japan) after 0 to 10 hours of incubation. For these tests, OD measurements were used because it offered a simple and reliable means of measuring the concentration of bacteria as a function of time. Three different aliquots from each solution were measured at each time, after which they were returned to their respective solutions. A reference solution containing only BHI broth culture medium and H<sub>2</sub>O was used to calibrate the instrument at 600 nm and create a baseline.

**2.5. Antibacterial Effects of Fluoride.** Sodium fluoride (NaF) powder (Sigma-Aldrich), H<sub>2</sub>O, and BHI broth were mixed to obtain 10 mL solutions with varying fluoride strength, from 0 to 2000 ppm. To each solution, 50  $\mu$ L of *S. mutans* suspension (OD<sub>600</sub> = 1.0) was added. Three samples at each fluoride concentration were incubated at 37°C for 8 h, after which OD measurements were made at 600 nm in the spectrophotometer.

**2.6. Statistical Analysis.** Using the statistical software package SPSS v19 (SPSS Inc., IL, USA), a univariate analysis of variance (ANOVA) was carried out to identify statistical differences in amount of viable cells after DCT on the different materials (cements and control) and after varying time. Multiple comparisons were made using the Sheffe's method, and differences were considered significant at the 95% confidence level ( $P < 0.05$ ).

### 3. Results

**3.1. Direct Contact Test.** The standard curve from the dilution series resulted in a linear relationship between the degree of fluorescence and the known amount of bacteria present. Figure 1 shows the corresponding relationship between the number of viable bacteria, labeled as colony forming units (CFUs) and fluorescence, measured in relative fluorescence units (RFUs). A linear fit to the data was used to calibrate fluorescence measurements from the test cements relative to the dilution series and was utilized in the results shown in Figure 2.

Figure 2 displays the number of viable bacteria for each material after the different aging times, where each bar is the average from six different wells. The strongest antibacterial activity was demonstrated by CA, which showed significantly different values from the control ( $P < 0.0005$ ) and all other

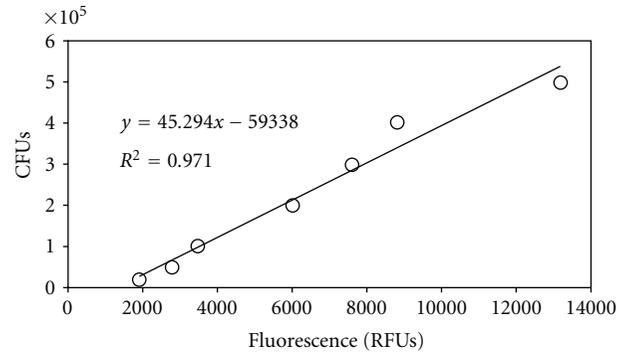


FIGURE 1: Relationship between CFUs and fluorescence, derived from the standard curve of serially diluted bacteria.

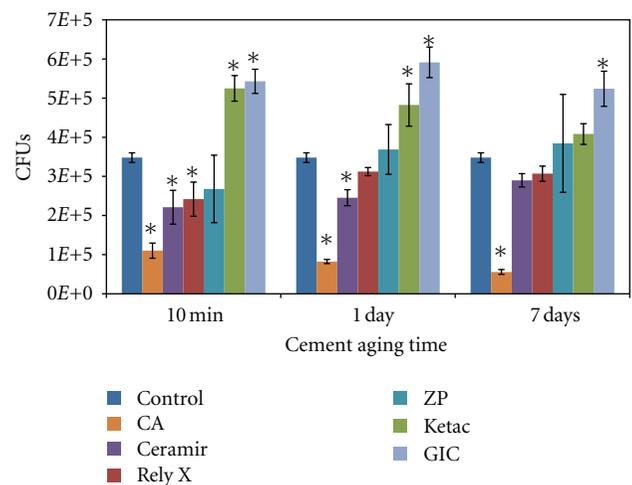


FIGURE 2: Amount of CFUs present in solution after direct contact tests. Significant differences ( $P < 0.05$ ) from the control (PMMA) are indicated by \*. Note: The first bar in each aging time group shows the same control PMMA data for each group since the PMMA samples were not aged.

cements ( $P \leq 0.014$ ) at all aging times. It also showed a significant decrease in CFUs with increased aging time ( $P \leq 0.006$ ). Ceramir showed antibacterial properties after 10 min and 1 day of aging ( $P \leq 0.004$ ) but was not significantly different from the control after 7 days of aging. RelyX also showed significant difference from the control after 10 min aging ( $P = 0.022$ ), but not after 1 day or 7 days. The remaining cements (ZP, Ketac and GIC) showed either higher number of viable bacteria or were not significantly different from the PMMA control at all instances.

**3.2. Antibacterial Effects of pH.** Effects of pH on bacterial proliferation are shown in Figures 3 and 4. The pH of the control and test solutions ranged from 1.5 to 9.0. No bacterial proliferation was seen at levels below pH 6.3 or above pH 9.0. *S. mutans* proliferated between pH 6.3 and 8.6 and showed strongest growth in the neutral pH buffer and in the H<sub>2</sub>O control. The curves are characterized by an initial lag phase (0–2 h), followed by a growth phase and a final stationary

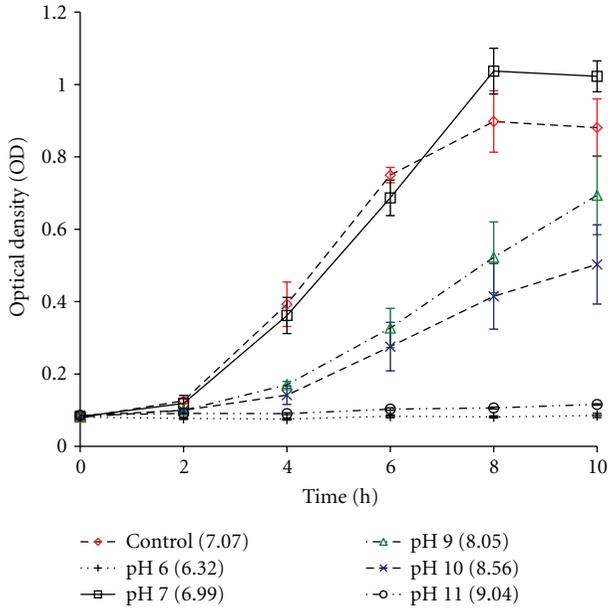


FIGURE 3: Growth curves of *S. mutans* in BHI at different pH buffer/BHI solutions. Value in brackets indicates the resulting pH of buffer/BHI solution.

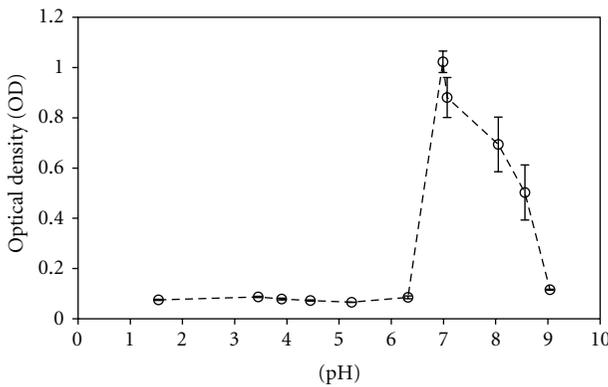


FIGURE 4: Amount of bacteria present in solution after 10 h incubation as a function of solution pH. Proliferation was seen at neutral and slightly basic levels.

phase. However, a considerable gap exists between the pH buffer 7 and H<sub>2</sub>O control in the latter part of the growth. This is likely due to the fact that as bacteria grow, acid is produced that will negatively affect the bacterial proliferation after approximately 6 h. The buffer, however, has the ability to regulate for this and proliferation continues until the stationary phase is reached at a later point.

**3.3. Antibacterial Effects of Fluoride.** Figure 5 displays the effect of fluoride on bacterial proliferation. A negative effect (i.e., reduction in the bacterial growth rate) was observed even at 200 ppm, with an increasing effect with increasing fluoride concentration until an approximately steady state was reached at roughly 1400 ppm.

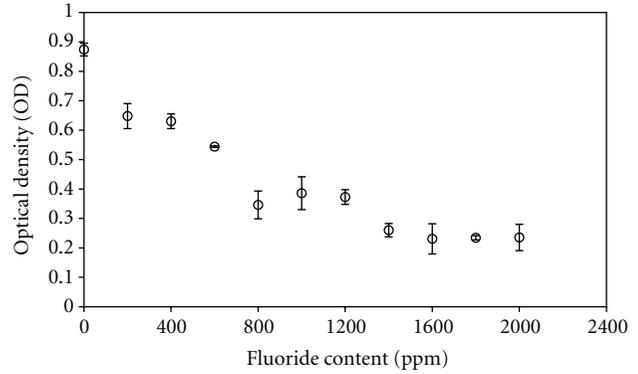


FIGURE 5: Amount of *S. mutans* present in solution as a function of fluoride content, measured by OD at 600 nm, after 8 hours incubation.

#### 4. Discussion

The longevity of dental restorations is often determined by their ability to resist plaque formation and consequently avoid secondary caries [2, 3, 20]. Although it has been suggested that early plaque formation is largely influenced by the intraoral positioning of restorations and general oral environment [4], cements having antibacterial properties could successfully prevent or delay caries formation and prolong the lifetime of restorations. In the current study, antibacterial properties of different classes of dental cements were investigated by means of a modified DCT. Previous studies have shown various glass-ionomer cements to have initial bactericidal properties due to low pH during curing or slow release of fluoride [7, 8, 10, 23], whereas another study showed polycarboxylate cement and zinc phosphate cement to be more active both initially and over time [9], which was attributed to low pH and fluoride release. In this study, the bioceramics CA and Ceramir exhibited the highest degree of antibacterial activity, followed by the RelyX resin cement. ZP showed some initial bacterial inhibition but was not significantly different from the PMMA control and displayed a large spread in data. The pure GIC and Ketac showed higher bacterial content than the PMMA control for all aging times, and the differences were significant in all cases except for Ketac after 7 days of aging.

Conventional luting cements that set by acid-base interactions produce an environment that is initially acidic, but approach neutrality during the course of the reaction. Low initial pH is recognized as beneficial with regards to bactericidal properties; however, this can have negative consequences as acid diffusion through thin dentin sections which can cause pulpal irritation has been reported for glass-ionomer and zinc phosphate cements [24]. The minimum pH for organisms such as *S. mutans* to grow is approximately 5 [25], and although this study showed clear inhibition from pH 6.3, none of the cements maintaining a pH below neutral after setting (Ketac, GIC, and ZP all end up around pH 6) displayed any clear bactericidal properties. RelyX showed some antibacterial properties after being aged for 10 min, but at that time should no longer be acidic. The light cured RelyX resin cement reaches pH 5 within minutes after onset of the

reaction and quickly continues to pH 8 before stabilizing at a neutral level after 24 h [26]. This means that the initial bactericidal effect of RelyX could potentially be attributed to fluoride release which is highest during the first 24 h [10]. However, GIC also releases fluoride and here no antibacterial effect was observed at any aging time, so it is not clear that fluoride gives an antibacterial effect.

Ceramir is also acidic during the first stages of the setting reaction, but quickly surpasses neutrality to reach basic levels. The pH of CA can reach over 12 during the reaction [27], but settles around 11.5 after final setting, while Ceramir stabilizes around 8.5 after roughly 12 hours. As shown in Figure 4, inhibition was also observed for higher levels of pH, and therefore the bactericidal properties displayed by Ceramir during initial setting times and especially by CA could be due to the basic environment they produce. Since the pH of Ceramir lowers after 12 h, it is also likely that another antibacterial mechanism, such as fluoride release, is responsible for the observed antibacterial effect.

Fluoride is not only widely used as an anticariogenic agent in common dental products such as toothpaste and mouthwash, it is also present in a wide range of restorative materials [10]. Among the cements investigated in the current study, fluoride is released from RelyX, Ceramir, Ketac, and GIC. However, within the limitations of the experiments performed, no conclusive evidence of antibacterial activity directly attributable to fluoride release from these cements could be shown. The anticariogenic effects of fluoride involve a variety of mechanisms, including inhibition of demineralization and enhancement of remineralization at the crystal surface as well as inhibition of bacterial growth and metabolism [6]. This discussion will, however, be limited to the action of fluoride on bacteria.

As seen in Figure 5, fluoride has a direct effect on bacteria proliferation. The decreasing OD with increasing fluoride concentration indicates that increasing fluoride concentration negatively affects the bacterial growth rate. Fluoride can act in various ways to stop or slow bacterial growth;  $F^-$  or HF can cause direct inhibition of enzymes such as enolase, urease, phosphatases, or heme catalase, which are all involved in microbial cell metabolism; metallic fluoride complexes such as  $AlF^-$  and  $BeF^- \cdot H_2O$  can effect enzymes and regulatory phosphates, with either positive or negative outcome for the cell; and HF can act as a transmembrane proton carrier to disturb the cell membrane through a  $\Delta pH$  discharge [25]. Direct inhibition of enzymes through binding of  $F^-/HF$  is a pH-dependent process, where  $F^-$  in many cases binds to sites normally occupied by  $OH^-$ , followed by binding to a proton.  $F^-$  has been shown to be unable to cross the cell wall and membrane, whereas HF passes unhindered [25]. Well inside the cell, HF dissociates to create an acid environment and releases  $F^-$ , which will accumulate and disturb the enzymes present [6]. In this case, HF acts as a proton carrier across the membrane and overloads the proton-extruding ATPases, as extruded protons will reenter as HF and eventually cause cell starvation and generally deenergize the membrane through the  $\Delta pH$  discharge.

It has been suggested that the ideal release profile of fluoride from dental cements should be characterized by an

initial burst, followed by a stable, lower release rate [28]. It should be noted that the amount of fluoride released from dental restoratives is far less than the amounts shown in Figure 5. Accumulated release varies between material types and products, but resin cements have been shown to have similar release profiles as resin-modified and conventional glass-ionomer cements, which are able to reach 15 ppm in the first week [20, 28, 29]. However, with the occurrence of shrinkage during setting, which allows gaps or voids to form between the cement and tooth, a strong initial fluoride release could increase fluoride concentration in the area, reducing the proliferation of bacteria and helping prevent secondary caries. A subsequent constant, lower level release of fluoride could aid in maintaining the resistance to bacteria and buildup of plaque and subsequent caries in sensitive areas.

Based on the results from the DCT in the current study, fluoride released from the cements could not be singled out as an antibacterial agent. Similar conclusions have been drawn for fluoride releasing restoratives by others [10, 20]. Nonetheless, it is possible that synergetic effects of fluoride with, for example, pH result in the observed bactericidal effects with luting agents such as Ceramir.

## 5. Conclusions

The antibacterial properties of four commercially available luting agents and two reference materials were tested in this study. Only calcium aluminate cement showed significant antibacterial properties compared to the PMMA control after aging for 10 min, 1 day, and 7 days. An increase in antibacterial effect was found for calcium aluminate cement with increased aging time. Antibacterial activity was also shown for Ceramir after 10 min and 1 day aging and for RelyX after 10 min aging. Cements having high rather than low pH after setting were shown to be more antibacterial, despite the fact that clear negative effects on bacteria proliferation were seen at pH levels below 6.3 and above 9.0. No correlation between either acidic materials or fluoride release and antibacterial properties could be seen; rather, basic materials showed the strongest antibacterial properties.

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## Review Article

# A Review of Luting Agents

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Due to the availability of a large number of luting agents (dental cements) proper selection can be a daunting task and is usually based on a practitioner's reliance on experience and preference and less on in depth knowledge of materials that are used for the restoration and luting agent properties. This review aims at presenting an overview of current cements and discusses physical properties, biocompatibility and other properties that make a particular cement the preferred choice depending on the clinical indication. Tables are provided that outline the different properties of the generic classification of cements. It should be noted that no recommendations are made to use a particular commercial cement for a hypothetical clinical situation. The choice is solely the responsibility of the practitioner. The appendix is intended as a guide for the practitioner towards a recommended choice under commonly encountered clinical scenarios. Again, no commercial brands are recommended although the author recognizes that some have better properties than others. Please note that this flowchart strictly presents the author's opinion and is based on research, clinical experience and the literature.

## 1. Introduction

Proper selection of a luting agent is a last important decision in a series of steps that require meticulous execution and will determine the long-term success of fixed restorations. One hundred years ago this decision was easy with the availability of essentially only one luting agent, zinc phosphate cement. Currently, a plethora of luting agents is available. Now the choice of the optimal luting agent can be confusing, even for the most experienced clinician. Restorations of metal, porcelain fused to metal, low- and high-strength ceramics, full or partial coverage, require a prudent approach and the proper cement selection should be based on knowledge of physical properties, biological properties and other attributes of both restorative materials and luting agents. This paper aims at providing an overview of currently available luting agents (cements) and discusses their advantages and disadvantages. Emphasis has been placed on composition, biocompatibility, physical properties, clinical indications, and clinical performance. A wide range of formulations has

been developed over the last 40 years, but here emphasis has been placed on the contemporary most frequently used ones, whether used for luting or bonding.

## 2. Classification of Cements

Cements can be classified as follows:

- (1) liners and bases;
- (2) temporary (provisional) cements;
- (3) permanent cements.

*2.1. Liners and Bases.* Preference seems to be given by the dental profession to visible light curing materials, in particular resin-modified glass ionomer (RMGI) cements (sometimes also referred to as resin reinforced glass ionomer (RRGI), when there is a need for a base or a liner. The reason is based on simplicity and on the fast setting characteristics

of light curing materials as well as the possibility of subsequently etching them in order to establish strong adhesive bonds with dentin bonding agents. Furthermore, they adhere well to unetched hard tissue and exhibit sustained fluoride release.

**2.2. Provisional Cements.** Provisional cements can be eugenol, noneugenol, resin, or polycarboxylate based. Caution has to be exercised when using eugenol-containing cements as the eugenol can contaminate the preparation. This can inhibit the polymerization of certain resin composites subsequently used as permanent restorative filling material [1].

Eugenol-containing temporary cements that are used prior to indirect bonding restorations reduce the bond strength of both total- and self-etching adhesive systems to dentin [2]. It is therefore advisable to use noneugenol temporary cements. In another report, however, no difference in bond strengths was observed when using eugenol-free and eugenol-containing provisional cements followed by self-adhesive resin cements [3].

Most subsequent publications report on a reduced bond strength of luting agents when eugenol-containing temporary cements are used [4, 5]. Nevertheless, the application of any temporary cement, whether eugenol-containing or not, contaminates the dentin, which will interfere with adhesion.

**2.3. Permanent Cements.** Figure 1 shows the chronological development of luting agents from the late 1800 hundreds to today. It is significant in that for almost 100 years only zinc phosphate cement was available, which is still being considered the “gold” standard.

With the introduction of cast restorations in the late 1880s, the need for a luting agent or dental cement for crowns and small bridges was readily recognized by the dental profession. The Dental Cosmos reported (in the late 1800s), a technique for the fabrication of a 4-unit pin ledge bridge (Finley), which required cement for fixation. While gold shell crowns were introduced around 1883 it was not until 1907 that Taggart introduced cast crowns by means of the lost wax technique. Around 1879, zinc phosphate cement was introduced and although the formulation has been refined during more than a century of use, it is a luting agent that has consistently been successful in clinical practice and even today is still considered the “gold” standard. With the exception of silicate cement in the 1940s few new cements were introduced until around 1970. The word silicate cement, however, is a misnomer as it was not a luting agent. It was used for anterior Cl III and Cl V esthetic restorations.

### 3. Zinc Phosphate Cement

The cement comes as a powder and liquid and is classified as an acid-base reaction cement. The basic constituent of the powder is zinc oxide. Magnesium oxide is used as a modifier ( $\pm 10\%$ ) while other oxides such as bismuth and silica may be present.

The liquid is essentially composed of phosphoric acid, water, aluminum phosphate, and sometimes zinc phosphate. The water content is approximately  $33 \pm 5\%$  and is an important factor as it controls the rate and type of powder/liquid reaction [6].

When the powder reacts with the liquid a considerable amount of heat is generated (exothermic reaction) and when the mixing is complete the cement reaches a pH of 3.5. Since the cement is placed on and in prepared teeth when it is in a “wet consistency” and not all the liquid has reacted with the powder, unreacted phosphoric acid liquid with a low pH  $\pm 1.5$  comes in contact with the preparation and causes an immediate (within 5 s) dissolution of the smear layer and smear plugs. Since cementation can cause a considerable amount of hydraulic pressure, the unreacted acid is pressed in the dentinal tubules and, depending on the remaining dentin thickness (RDT), the distance from the floor of the preparation to the pulp, can cause greater or less irritation to the pulp. Therefore, the pulp has to cope with not only heat but low acidity as well. The greater the RDT, the more beneficial the buffering action of the fluid in the dentinal tubules is and the less the effect of the acid. Furthermore, a greater RDT also diminishes the thermal effect. When fully reacted, the set cement reaches a pH = 6.7 after 24 hours. Postcementation hypersensitivity is indeed a frequently occurring clinical problem, which either resolves over time or may result in the need for endodontic treatment. If it resolves, it is through the protective action of secretion of secondary dentin by the odontoblasts, which increases the RDT. This however, does not start in humans until 3 weeks after the insult has taken place and deposition of secondary dentin occurs in microns per day [7]. If the irritation cannot be handled by the body, the pulp becomes necrotic, which then requires root canal treatment. Therefore, although the set luting material may be biocompatible, postcementation discomfort is a known unfavorable side effect when using this cement. Attempts at blocking access of the unreacted phosphoric acid to the dentinal tubules have been made in the form of a varnish (Copalite). Unfortunately, Copalite can reduce the retention of the restoration by as much as 50% [8].

### 4. Zinc Polycarboxylate Cement

Polycarboxylate cement is also an acid-base reaction cement. The powder is composed of mainly zinc oxide, magnesium oxide, bismuth, and aluminum oxide. It may also contain stannous fluoride, which increases strength. The liquid is composed of an aqueous solution of polyacrylic acid or a copolymer of acrylic acid and other unsaturated carboxylic acids. Fluoride release by the cement is a small fraction (15–20%) of that released from materials such as silicophosphate and glass ionomer cements.

When mixed at the recommended P/L ratio the final mix appears more viscous than zinc phosphate cement. However, this can be offset by vibratory action during seating yielding a film thickness of  $\pm 25 \mu\text{m}$ . At no time should the amount of liquid be increased, as it will adversely affect

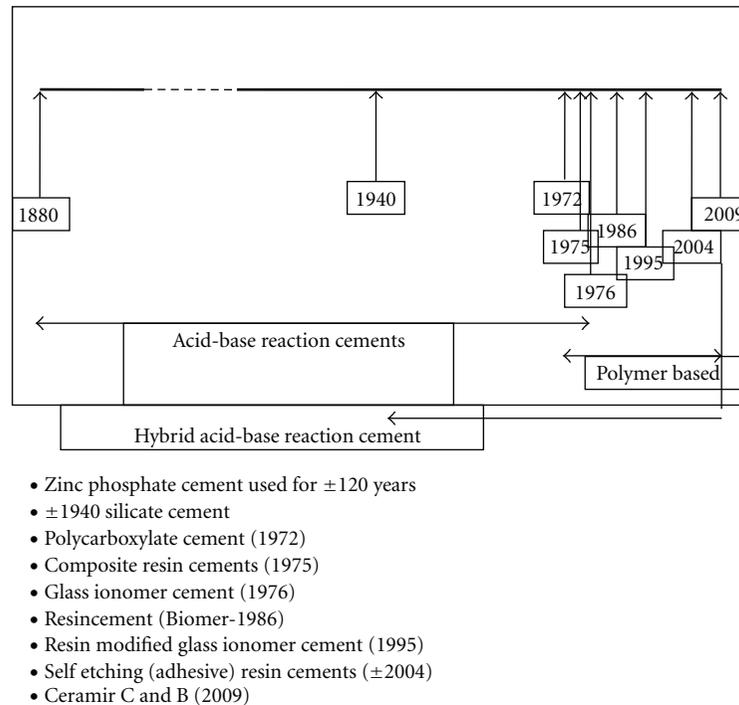


FIGURE 1: An overview of the chronological development of luting agents starting around 1880 until today. The last 30–40 years have witnessed the development of new cement systems and a large number of cements have become available. It was not until 2009 that a paradigm shift took place and a hybrid acid-base reaction cement was introduced, which offered physical and other properties that not only differed from the polymer-based luting agents but also matched them. ±1880—zinc phosphate cement, ±1940—silicate cement\*, 1972—polycarboxylate cement, ±1975—composite resin cements, 1976—glass ionomer cement, 1986—resin cement, ±1995—resin-modified glass ionomer cement, ±2004—self-etching (adhesive) resin cements, 2009—hybrid-acid-base reaction cement, (\*the designation silicate cement is a misnomer as it was a restorative material for CI III and CI V restorations).

the compressive strength, which at 55 MPa is already lower than that of zinc phosphate cement. Biological properties of polycarboxylate cement are quite favorable and the cement causes little or no irritation to the pulp, even at a remaining dentin thickness of 0.2 mm (Unpublished data). It is believed that the long molecular chains of the polyacrylic acid prevent penetration into the dentinal tubules. It is of interest to note that both zinc phosphate and polycarboxylate cements have a pH of about 3.5 immediately after mixing. Currently polycarboxylate cements are mostly used for long-term temporary cementation.

Polycarboxylate and glass ionomer cements exhibit a property that is called chelation, which is the ability to bond to the Ca ions.

## 5. Glass Ionomer Cement

Glass ionomer cements (GICs) were invented in the late 1960s in the laboratory of the Government Chemist in Great Britain and were first reported on by Wilson and Kent in 1971 [9]). GICs set by means of chelation as a result of an acid-base reaction. They strongly adhere to enamel and to some extent to dentin and release fluoride. Initially used as a restorative

material, GI further evolved into a luting agent, which is now the predominant application of this class of material.

The powder consists of aluminosilicates with high fluoride content. The material is formed by the fusion of quartz, alumina, cryolite, fluortite, aluminum trifluoride, and aluminum phosphate at temperatures of 1100–1300°C. This glass frit is cooled to a dull glow and quenched in water. It is subsequently ground into 45 μm particles.

The liquid is composed of polyacrylic acid and tartaric acid, the latter to accelerate the setting reaction. The reaction of the powder with the liquid causes decomposition, migration, gelation, postsetting hardening and further slow maturation. The polyacrylic acid reacts with the outer surface of the particles resulting in release of calcium, aluminum, and fluoride ions. When a sufficient amount of metal ions has been released, gelation occurs, and hardening continues for about 24 hours [9].

GIC display a relatively low curing shrinkage; within the first 10 minutes 40–50% of shrinkage has occurred.

However, with the use of GIC as a luting agent, frequent postcementation sensitivity has been reported. The then accepted ANSI/ADA Specification 41, Recommended Standard Practices for Biological Evaluation of Dental Materials

stipulated that luting agents should be tested for pulp reaction in primates by passively inserting a heavier than luting consistency mix in Class V restorations in primates. Indeed the results of these tests demonstrated that the cement was biocompatible and nonirritating [10]. In a subsequent study, also in primates, crowns were cemented adhering to a clinically more relevant cementation protocol, with a cement mix that had a normal luting consistency [11].

In this study hydraulic pressure generated during cementation and the resulting penetration of unreacted acid into the dentinal tubules was responsible for the true postcementation reaction of the pulp under clinical conditions. It was clearly demonstrated that, depending on the RDT, GIC caused pulpal inflammation which, rather than subsiding over time, increased in severity. It was this study that resulted in a change in protocol in the ANSI/ADA Specification 41 (2005) [12], which now calls for a pressure insertion technique. Rather than using a laborious indirect technique and cementing all metal cast crowns as was done in the aforementioned study, Class V composite resin inlays are fabricated and cemented with the cement to be tested. With the use of this technique, hydraulic pressure is generated that is similar to complete crown cementation. In addition, the Class V inlays are usually closer to the pulp than crown preparations and therefore result in a more reliable biocompatibility reaction.

## 6. Resin Cements

As an alternative to acid-base reaction cements, resin cements were introduced in the mid-1980s, these materials have a setting reaction based on polymerization. Resin cements are polymers to which a filler has been added as well as fluoride. Cement film thickness is not favorable for some materials, for example, C & B Metabond (Parkell Inc.) with a film thickness  $> 100 \mu\text{m}$ , while others have a reported film thickness of  $9 \mu\text{m}$ , for example, Permalute (Ultradent Products Inc). One of the first resin cements was marketed by Dentsply/Caulk under the name Biomer, around 1987. In two clinical studies by Pameijer (unpublished data), the cement performed well over a one-year period of evaluation. However, over time polymer degradation occurred due to hydrolysis, while a lack of bonding to enamel and dentin made the cement unsuitable as a stand-alone luting agent, leading to leakage and failure of the restoration. Additionally, incomplete polymerization can lead to irritation of the pulp by unreacted monomers.

In combination with a dentin bonding agent, however, many resin cements have superior properties and are frequently used for the cementation (bonding) of porcelain laminate veneers. The concept of a "monobloc" described in endodontics [13] applies here as well. A combination bonding agent that bonds to tooth structure and a resin cement that adheres to the bonding agent and to silane treated porcelain follows the same principles. Nevertheless, there is a reluctance on the part of practitioners to do a "total etch" of complete crown preparations, which is a required step for many bonding agents. Even the self-etching

dentin bonding agents are not ideal because of concerns for postoperative sensitivity.

## 7. Resin-Modified Glass Ionomer (RMGI) Cements

The RMGI or RRG (resin-reinforced glass ionomer) cements are indicated for the luting of crowns and bridges, as well as inlay and onlay restorations. They are essentially hybrid formulations of resin and glass ionomer components. The RMGI cements are relatively easy to handle and are suitable for routine application with metal-based crown and bridgework. However, their use is limited when adhesively cementing ceramics with smooth, nonretentive surfaces. Adhesion to tooth structure is not strong with these materials. Additionally, some early formulations have displayed excess water sorption, causing swelling frequently resulting in ceramic fracture. Commercial examples of the RMGI cements are: RelyX Luting, RelyX Luting Plus (3M/ESPE), Fuji Plus (GC) and UltraCem RRG Luting Cement.

In a recent article, the biological effects of resin-modified glass-ionomer cements as used in clinical dentistry were described, and the literature reviewed on this topic [14]. Information on resin-modified glass ionomers and on 2-hydroxyethyl methacrylate (HEMA), the most damaging substance released by these materials, was collected from over 50 published papers. These were mainly identified through Scopus. It is known that HEMA is released from these materials, which has a variety of damaging biological properties, ranging from pulpal inflammation to allergic contact dermatitis. These are therefore potential hazards from resin-modified glass ionomers. However, clinical results with these materials that have been reported to date are generally positive. According to the above authors, RMGIs cannot be considered biocompatible to nearly the same extent as conventional glass-ionomers. Care needs to be taken with regard to their use in dentistry and, in particular, dental personnel may be at risk from adverse effects such as contact dermatitis and other immunological responses. Interestingly, RMGIs have a better clinical track record than glass ionomer cements.

In general few complaints have been reported about postoperative cementation hypersensitivity. Yet, RMGIs are in the category of resin cements and water sorption and degradation through hydrolysis are negative features that should not be ignored or underestimated.

In spite of the numerous research methodologies that are at our disposal conflicting results are frequently reported, either using the same technique and tests on the same materials, or using different techniques and testing the same materials. RMGIs as shown above are such an example. While controversial data has been generated, successful clinical use seems to contradict these findings.

## 8. Adhesive Resin Cements

The poor adhesive properties of the RMGIs have led to further development of resin-based luting agents, which

have resulted in the introduction of adhesive resin cements. These cements do not require pretreatment and bonding agents to maximize their performance. In order for these cements to be self-adhesive, new monomers, filler and initiator technology were created. Examples of these materials are: MaxCem (Kerr), RelyX Unicem (3M/ESPE), Breeze (Pentron), Embrace Wet Bond (Pulpdent Corporation) to name a few. These cements enjoy great popularity as they have universal applications. As pointed out before under resin and RMGI cements, polymer degradation over time is still an issue. Matrix metalloproteinases (MMPs) are fossilized within mineralized dentin and can be released and activated during bonding [15]. These endogenous collagenolytic enzymes are on the collagen fibers and needed for bonding and their slow degrading enzymatic action is beyond the control of even the most meticulous clinician. Reports have appeared that recommend pretreatment of the dentin with 2.0% chlorhexidine gluconate with a pH of 6.0, which prevents the action of the endogenous enzymes [16].

## 9. Hybrid-Acid-Based CaAl/Glass Ionomer

Only one formulation is presently known that is based on calcium aluminate/glass ionomer. Ceramir C&B (Doxa Dental AB, Uppsala, Sweden) is a new dental luting agent intended for permanent cementation of crowns and bridges, gold inlays and onlays, prefabricated metal, and cast post and cores and all-zirconia or all-alumina crowns. The cement is a water-based hybrid composition comprising of calcium aluminate and glass ionomer components that is mixed with distilled water. The material has been demonstrated to be bioactive [17]. The setting mechanism of Ceramir C&B is a combination of a glass ionomer reaction and an acid-base reaction of the type occurring in hydraulic cements. The incorporation of the calcium aluminate component provides several unique properties compared to conventional GIC's. There are several features that strongly contribute to the biocompatibility profile of the material. These include the fact that after setting, the material is slightly acidic, pH ~4. After 1 h, the pH is already neutral and after 3-4 hrs it reaches a basic pH of ~8.5. This means that the fully hardened material is basic and stays basic throughout its service. This basic pH is the most important prerequisite for the material to be bioactive, that is, creating apatite on its surface when in contact with phosphate-containing solutions [17]. The apatite forms during hardening but its formation continues when the hardened material is in contact with phosphate solutions. The basic pH is also an important factor in the biocompatibility profile of the material. Additionally, the material produces an excess of  $\text{Ca}^{2+}$  ions, which also contributes to its bioactivity. The incorporation of calcium aluminate fixes the GIC structure and hinders the ionomer glass from continuously leaking over time. Ceramir C&B has an initial fluoride release comparable to a glass ionomer, although the release tapers off over time. Unique properties such as apatite formation and remineralization develop quickly and continue to be active.

## 10. Pulpal Reactions

Ultimately, a postcementation pulpal reaction under clinical conditions is dependent on three factors:

- (1) composition of the cement. Postoperative hypersensitivity for most cements can be problematic and is based on their chemistry, while only a few do not present a problem;
- (2) the RDT—the larger the RDT the less risk of pulp irritation due to the greater buffering capacity of the fluid in the dentinal tubules;
- (3) time elapsed from preparation to moment of cementation—the longer this period, the better the pulp is able to recover from the trauma of preparation and therefore can tolerate a subsequent irritation better.

## 11. Biocompatibility

Luting agents for permanent cementation of crown and bridge restorations have to meet many requirements before they can safely be used in humans. The ANSI/ADA Recommended Standard Practices for Biological Evaluation of Dental Materials, Specification 41 (2005) [12], and the ISO 7405 provide a road map outlining tests that are required in order to meet these requirements. Physical properties such as hardness, flexural strength, and solubility are extremely important but if the material lacks biocompatibility, excellent physical properties are meaningless. For practitioner and patient alike, a luting agent that causes no postcementation hypersensitivity is highly desirable. Dentistry is still perceived by many, as being “a painful experience” and every effort should be made on the part of the dentist to make the treatment as comfortable as possible. One such step is the final cementation of a fixed crown and bridge work, whether a single unit or a bridge. A restoration may be esthetically pleasing and functional at the time of cementation, but a sequel of postcementation hypersensitivity can generate questions from the patient as to the success of the treatment, time from the practitioner to address the problem, and possible complications that require further treatment. Extra visits may be required, all of which constitute a loss of time and money not only for the practitioner, but also for the patient.

Although zinc phosphate cement is still the “gold” standard, advances in luting agents over the last 30 years have produced new luting agents, which most likely will eventually replace zinc phosphate cement altogether. If we look at the three acid-base reaction cements, zinc phosphate, polycarboxylate and glass ionomer cement and compare them to the hybrid-acid-base reaction cement, two of the three cements (zinc phosphate and glass ionomer cements) have well recognized postcementation hypersensitivity problems. This has frequently resulted in the need for root canal treatment after permanent cementation of the fixed unit. Typical complaints of a patient are sensitivity to hot and cold and chewing. Assuming that the occlusion is not a causative factor, the only explanation is irritation caused by the cement. Clearly, if the patient was comfortable during

TABLE 1: This Table compares properties of the various generic cements. (Biocomp: biocompatibility; Integr: integration, Oxy inh layer: oxygen inhibited layer, RRGI: resin reinforced glass ionomer).

Cement	Universal	Retention	Biocomp	Sensitivity	Integr	Self-Etch	Self-Seal	Bioactive	Oxy inh layer
Zinc Phosph	No	Low/med	*	Yes	No	No	No	No	No
Polycarb	No	Low	****	No	No	No	No	No	No
Glass ion	No	Medium	***	Yes	No	No	No	No	No
Resin	No	Medium	***	No	No	No	No	No	Yes
RRGI	Yes	Med/high	***	?	No	No	No	No	yes
Self-etch resin cement	Yes	High	****	?	?	Yes	No	No	Yes
Hybrid CaAl/GI	Yes	High	*****	No	Yes	Yes	Yes	Yes	No

TABLE 2: Comparison of additional properties of the various generic cements.

Cement	Nano crystals	Hydroxy apatite	Hydrolysis	Water sorption	Resin-based	Mineralizing	F-release
Zinc Phosph	No	No	No	No	No	No	No
Polycarb	No	No	No	No	No	No	No
Glass ion	No	No	No	No	No	Yes	Yes
Resin	No	No	Yes	No	Yes	No	Yes
RRGI	No	No	Yes	Yes	Yes	No	Yes
Self-etch resin cement	No	No	Yes	Yes	Yes	No	Yes
Hybrid CaAl/GI	Yes	Yes	No	No	No	Yes	Yes

the interim with a provisional restoration the problems point towards the irritation caused by the permanent cement. Mostly the pain will subside, more so with zinc phosphate cement than glass ionomers, but this may take weeks or longer, and the practitioner can only guess at the ultimate outcome. *In vivo* research has shown that indeed after cementation with zinc phosphate cement and glass ionomers causes pulpal irritation, which would explain the complaints from patients [11].

RMGIs also have a record of occasional postcementation hypersensitivity due to their questionable biocompatibility [14]. In particular, unreacted monomers are highly toxic and irritating.

The resin cements and self adhesive resin cements have a good track record, although there are few, if any, reports that support their biocompatibility.

Little clinical data are available on self-adhesive cements. Empirical data suggest that they are tolerated by the pulp, perhaps based on the change in acidity upon complete setting.

The many properties that are exhibited by luting agents are summarized in Tables 1 and 2.

Tables 1 and 2 clearly show the differences between the various generic cements. It is therefore important that the practitioner is familiar not only with the composition and properties of the luting/bonding agent, but also with the composition of the restoration to be cemented.

A separate flow chart is being presented in the appendix, which serves as a guide for the practitioner in the selection of a final luting agent. Hypothetical clinical situations are being presented that can be cross-referenced with a choice of a generic cement. The chart is based on clinical observations, research, and the literature.

## 12. Concluding Remark

The choice of an appropriate luting agent (cement) for final cementation of fixed crown and bridge units needs careful consideration as the ultimate success to a large extent depends on the correct choice.

## Appendix

See Table 3.

TABLE 3: Clinical indications for use of luting agents.

	(1) Single PFM 3-Unit bridge no sensitivity during interim good retention	(2) Single PFM 3-Unit bridge sensitivity during interim good retention	(3) Single PFM 3-Unit bridge no sensitivity during interim poor retention	(4) Single PFM 3-Unit bridge sensitivity during interim poor retention	(5) Large bridge no sensitivity during interim good retention	(6) Large bridge sensitivity during interim good retention	(7) Large bridge no sensitivity/ sensitivity during interim poor retention	(8) All ceramic, inlay, onlay, crown (pressable)	(9) Implant crown	(10) (1) Cast P&C (2) Prefab P&C (3) Fiber post	(11) High strength ceramics
Zinc phosphate	OK	NO	NO	NO	OK	NO	NO	NO	OK	(1) Good choice (2) Good choice (3) NO	NO
Glass ionomer	Good choice	NO	OK	NO	OK	NO	NO	NO	Good Choice	(1) OK (2) OK (3) NO	OK
Resin cement	Good choice with DBA	NO	Good choice with DBA	NO	OK with DBA	NO	NO	Good Choice with DBA	OK	(1-3) Good choice with DBA	OK with DBA
Resin modified glass ionomer	Good choice	OK	Good choice	OK	Good choice	OK	OK	NO	OK	(1-3) OK	OK
Self-etching resin cement	Good choice	OK	Good choice	OK	Good choice	OK	Good choice	OK	Good Choice	(1-3) OK	Good choice
CaAl hybrid	Good choice	Good choice	Good choice	Good choice	Good choice	Good choice	Good choice	NO	Good choice	(1) Good choice (2) Good choice (3) NO	Good choice

Good choice  
 OK, but better choices are available  
 NO

DBA: Dentin bonding agent NECESSARY. increases retention and provides a seal.

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## Review Article

# Adhesion and Cohesion

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The phenomena of adhesion and cohesion are reviewed and discussed with particular reference to dentistry. This review considers the forces involved in cohesion and adhesion together with the mechanisms of adhesion and the underlying molecular processes involved in bonding of dissimilar materials. The forces involved in surface tension, surface wetting, chemical adhesion, dispersive adhesion, diffusive adhesion, and mechanical adhesion are reviewed in detail and examples relevant to adhesive dentistry and bonding are given. Substrate surface chemistry and its influence on adhesion, together with the properties of adhesive materials, are evaluated. The underlying mechanisms involved in adhesion failure are covered. The relevance of the adhesion zone and its importance with regard to adhesive dentistry and bonding to enamel and dentin is discussed.

## 1. Introduction

Every clinician has experienced the failure of a restoration, be it loosening of a crown, loss of an anterior Class V restoration, or leakage of a composite restoration. The procedure is much the same for any such failure, namely, removal of residual adhesive or luting agent and recementation of the restoration. The clinical notes will describe the problem as, commonly, adhesive or cohesive failure based on a simple classification system such as that in Figure 1. The causes of such failures are seldom addressed by most clinicians.

Adhesion and cohesion are terms that are often confused although these subjects are discussed in many standard texts in dental biomaterials science [1–3]. There are also many excellent texts and monographs on adhesion, cohesion, and interfacial reactions [4–6] together with a comprehensive treatment in the on-line encyclopedia, Wikipedia. Since adhesion and cohesion play a very important role in the use of luting agents, an in-depth discussion is appropriate in view of the communications presented in this issue.

The Merriam-Webster dictionary has several definitions of the word “adhesion” but the most apposite here is *the molecular attraction exerted between the surfaces of bodies in contact*. This dictionary likewise has several definitions of the word “cohesion” but the most pertinent here is *the*

*molecular attraction by which the particles of a body are united throughout the mass*. In other words, adhesion is any attraction process between dissimilar molecular species, which have been brought into direct contact such that the adhesive “clings” or binds to the applied surface or substrate. The postsurgical complication of adhesions, involving soft tissues, will not be discussed here.

In contrast, cohesion is an attraction process that occurs between similar molecules, primarily as the result of chemical bonds that have formed between the individual components of the adhesive or luting agent. Thus, cohesion may be defined as the internal strength of an adhesive due to various interactions within that adhesive that binds the mass together, whereas adhesion is the bonding of one material to another, namely, an adhesive to a substrate, due to a number of different possible interactions at the adhesive-substrate surface interface. These differences are shown schematically in Figure 2. In dentistry, when a restoration is cemented or bonded to a tooth, adhesive forces bind the luting agent to the restoration on one side and to the tooth on the other side with cohesive forces operating within the luting agent itself, Figure 3.

The characteristics of chewing and bubble gums clearly indicate the difference between cohesion and adhesion. Gum holds together during mastication because of good cohesion

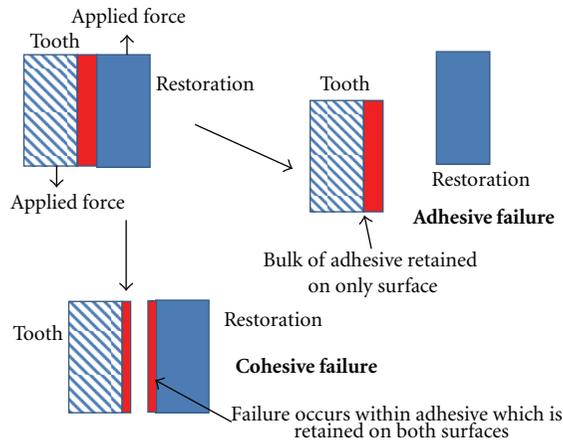


FIGURE 1: Adhesive and cohesive joint failures.

and, in the case of bubble gum, enables the gum to be blown into a bubble. These materials, however, exhibit poor adhesion in that they do not readily stick to the teeth, oral tissues, or other surfaces, unless mechanical effects intervene. If, for example, gum while being chewed can lodge into undercuts or between teeth, it can get locked in and may be torn away from the bulk of the gum, that is, mechanical interlocking of the gum within the interproximal area is greater than the cohesive strength of the gum. Likewise, chewed gum does not stick well to smooth surfaces such as glass or polished metal because of its poor adhesion. However, if the masticated and softened gum is pressed onto a rough surface, the gum will distort and flow into gaps, rugosity and voids in the surface such that it “sticks,” often very tightly, to that surface, as most of us know when we try to scrape discarded gum off the soles of our shoes.

Likewise, zinc phosphate cement has good cohesive strength but exhibits poor adhesion to smooth surfaces. In particular, it does not bond, chemically to surfaces and its bonding or adhesion, that is, its application as a luting agent, is possible only through mechanical interlocking at the interface with the restoration and that with the tooth. Zinc phosphate cement, however, does possess good cohesive strength, even in thin films, so that when used as a luting agent for restorations subject to high masticatory stresses, it can support elastic deformation [7].

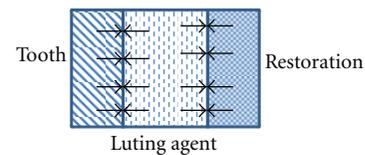
In every situation involving an adhesive and a substrate, the combination of adhesion and cohesion determines the overall bonding effectiveness. The adhesive bond will fail if the adhesive separates from the substrate or there is internal breakdown of the adhesive (i.e., cohesive failure), Figure 1.

## 2. Forces in Cohesion

The cohesive strength of a luting agent or adhesive, regardless of its chemical composition, is determined by a number of molecular forces:

- (1) the chemical bonds within the adhesive material,

Adhesion: attractive forces operate at interface between dissimilar surfaces



Cohesion: internal strength of a material

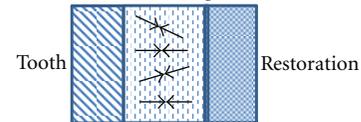


FIGURE 2: Adhesion and cohesion.

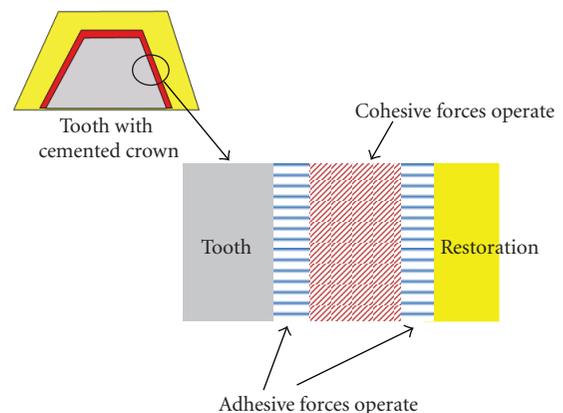


FIGURE 3: Adhesive and cohesive forces operating within a cemented restoration.

- (2) chemical bonds due to crosslinking of the polymer(s) within a resin-based material,
- (3) intermolecular interactions between the adhesive molecules, and
- (4) mechanical bonds and interactions between the molecules in the adhesive.

These molecular interactions, really intermolecular forces, affect the properties of the uncured (unset) adhesive, typically the consistency, flow properties, and viscosity of the adhesive. When the adhesive sets or “cures” to a solid mass, solidification occurs through bonds formed between the molecules in the adhesive, through formation of new bonds and by strengthening of existing bonds. This overall process typically consists of crosslinking of short chain molecules to form longer chains and/or formation of 3-dimensional networks of molecular chains. The latter is the common mechanism involved in the setting of zinc oxide-based dental cements. It follows from this that the cohesive strength of an adhesive is significantly affected by the curing conditions and, when curing/setting occurs under suboptimal conditions, the adhesive will lack cohesive strength.

Suboptimal conditions during the setting or solidification process is a common concern in restorative dentistry

and all luting agents, regardless of composition and characteristics, must be protected against the effects of oral fluids prior to and during the curing process to avoid detrimental effects on the setting reactions. Ingress of saliva and oral fluids into the adhesive during the setting process will adversely affect the curing reactions of both inorganic and organic adhesive materials, commonly reducing strength, bonding efficiency and the degree of cure. Thus, fluid ingress will not only imperil the integrity and efficacy of the adhesive-substrate interactions at both the tooth and restoration interfaces but also decrease the cohesive strength of the adhesive. The latter effect is important because the maximum load a bond can withstand in clinical practice as well as in laboratory strength tests may be dictated primarily by the cohesive strength of the adhesive, that is, under loading, the bond fractures due to cohesive failure of the adhesive rather than failure of the adhesive-substrate bond. In other words, the cohesive strength of the adhesive, and not the adhesion between adhesive and the substrate, may be the limiting factor in bond strength tests and in clinical practice.

### 3. Forces in Adhesion

Adhesion is the propensity of dissimilar particles and/or surfaces to adhere or bond to one another and can be divided into three basic types, Table 1. Specific adhesion is achieved through molecular interactions between the adhesive and the substrate surface. The intermolecular forces produce specific adhesion although this can really be divided into three different types, namely, chemical adhesion, dispersive adhesion, and diffusive adhesion, to which are added mechanical effects in effective adhesion. However, a distinction must be made between weak intermolecular interactions and strong chemical bonds. Although chemical bonds can form in a few substrate/adhesive combinations, for example, epoxy resin and aluminum, they are generally uncommon in dentistry except for those that occur between carboxylate-based luting agents and the calcium within dental hard tissues. When there are chemical bonds within the adhesive joints, they can account for up to 50% of all interactions although the long-term stability of these bonds is usually dependent on their resistance to moisture.

In addition to the intermolecular and chemical adhesion forces, micromechanical adhesion also can be involved in the overall adhesion phenomenon. In such cases, the adhesive can effectively cling to a roughened substrate surface and increase overall adhesion, for example, chewing gum attached to the soles of our shoes.

### 4. Mechanisms of Adhesion

The strength of the adhesion between two materials depends on the interactions between the two materials, and the surface area over which the two materials are in contact. As a result, a number of factors enter into the overall adhesion system.

*4.1. Contact Angle and Surface Tension.* Materials that wet against each other tend to have a larger contact area than

those that do not, however, wetting depends on the relative surface energies of the adhesive and substrate materials. Low surface energy materials such as poly(tetrafluoroethylene) or PTFE and silicone materials do not wet and are resistant to adhesive bonding without special surface preparation, hence the use of these polymers to manufacture nonstick cookware and other nonstick surfaces.

Wetting is the ability of a liquid to form an interface with a solid surface and the degree of wetting is evaluated as the contact angle  $\theta$  formed between the liquid and the solid substrate surface. This is determined by both the surface tension of the liquid and the nature and condition of the substrate surface. The smaller the contact angle and the lower the surface tension of the liquid, the greater the degree of wetting, that is, the droplet of liquid will spread across the substrate surface provided the latter is clean and uncontaminated, as shown in Figure 4. A clean surface allows good wetting, that is, the contact angle  $\theta$  is close to  $0^\circ$ , Figure 4(a). There will be a greater contact angle ( $\theta$  is greater than  $0^\circ$  but less than  $90^\circ$ , i.e.,  $0^\circ < \theta < 90^\circ$ ) with a slightly contaminated surface, Figure 4(b), and the contact angle between the liquid and a contaminated surface or one with low surface energy will exceed  $90^\circ$ , Figure 4(c). The latter condition is sometimes referred to as dewetting and the liquid will form droplets on the substrate surface.

The contact angle  $\theta$  is a function of both dispersive adhesion (the interaction between the molecules in the adhesive and those of the solid, as discussed later) and the cohesion within the liquid adhesive. If there is strong adhesion to the substrate surface and weak cohesion within the liquid, there is a high degree of wetting, often termed lyophilic conditions. Conversely, a combination of weak adhesion and strong cohesion, referred to as lyophobic conditions, results in high contact angles and poor wetting of the substrate surface, that is, droplets form on the surface rather than a film of fluid.

A small contact angle indicates more adhesion is present because there is a large contact area between the adhesive and the substrate, resulting in a greater overall substrate surface energy and a high interactive force between the liquid and the substrate.

These relationships can be put in another way. When the surface is wetted, the contact angle is less than  $90^\circ$  ( $\theta < 90^\circ$ ), the substrate has high surface energy and the adhesion forces between substrate and liquid are greater than the cohesive forces within the adhesive (i.e., the surface tension of the liquid,  $\gamma$ ) and the liquid can spread over the substrate surface. If the surface has low energy (or is contaminated),  $\theta > 90^\circ$  and cohesion within the adhesive can exceed the adhesion between liquid and substrate such that there is poor wetting or dewetting, with the liquid forming droplets on the surface.

Surface scientists express things in a different way and refer to interfacial tension using the terms liquid-air interfacial tension,  $\gamma_{LA}$  (i.e., the liquid's surface tension), solid-liquid interfacial tension,  $\gamma_{SL}$  (i.e., the surface tension between the solid and the liquid, which approximates to the surface adhesion between liquid and solid) and the solid-air interfacial tension,  $\gamma_{SA}$  (i.e., the surface tension between the

TABLE 1: Basic types of adhesion.

Type	Characteristics
Specific	Molecular attraction between surfaces in contact
Mechanical	Adhesion arising from mechanical interlocking between the adhesive and the substrate surface
Effective	Optimal bonding between adhesive and substrate surface due to combined effects of specific and mechanical adhesion

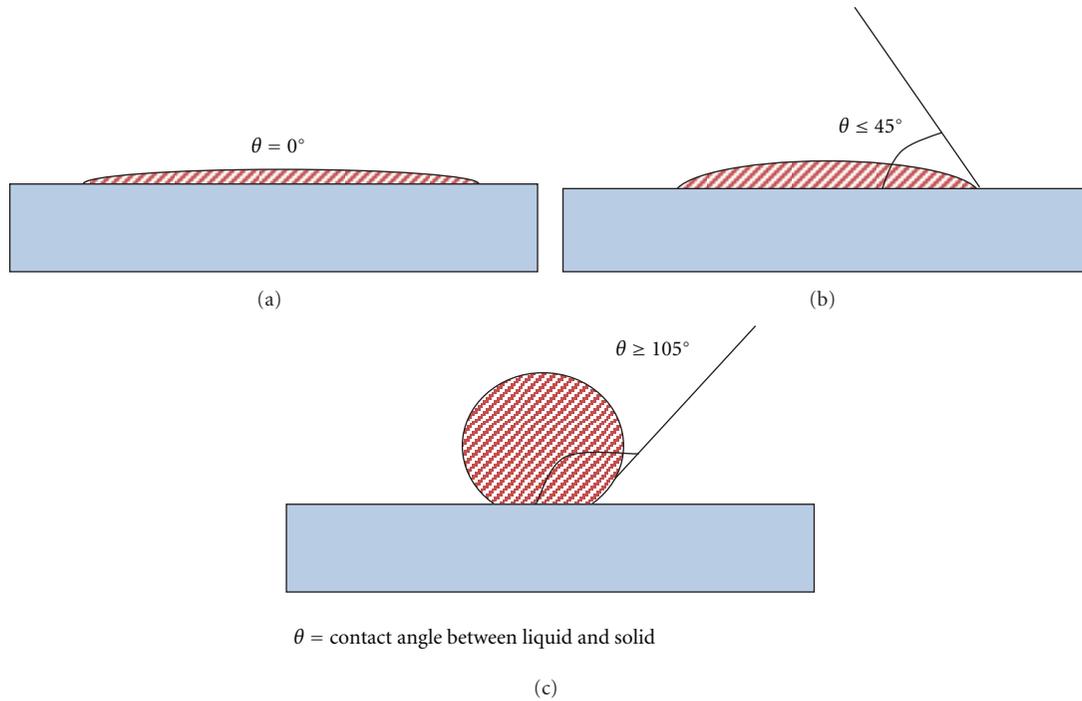


FIGURE 4: Liquid/surface contact angles for clean, slightly contaminated, and contaminated surfaces.

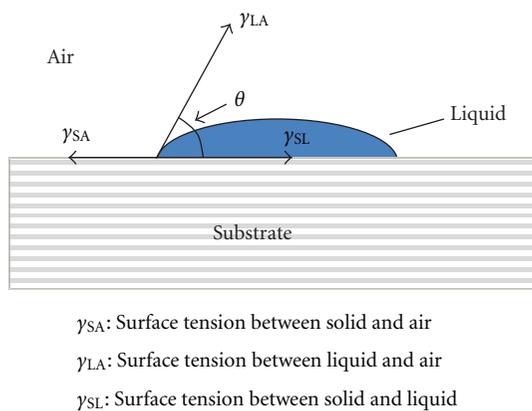


FIGURE 5: Interfacial tensions for a drop of liquid on a surface.

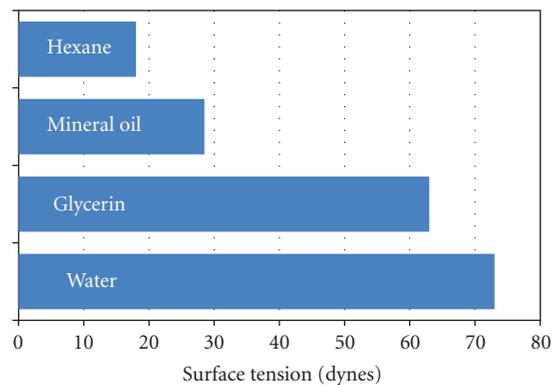


FIGURE 6: Surface tensions of common liquids.

solid and air, which approximates to the surface energy of the solid), Figure 5.

Surface tension is commonly expressed as dyne/cm, although it should really be given in the recommended SI units of N/m or J/m<sup>2</sup>. Figure 6 indicates the relative surface tensions of some common liquids.

For a contact angle of  $\theta^\circ$ , these entities are related by Young's equation,

$$\gamma_{LA} \cdot \cos \theta = \gamma_{SA} - \gamma_{SL} \tag{1}$$

If there is complete wetting of the substrate surface, that is, when  $\theta = 0$  and  $\cos \theta = 1$ , Young's equation indicates

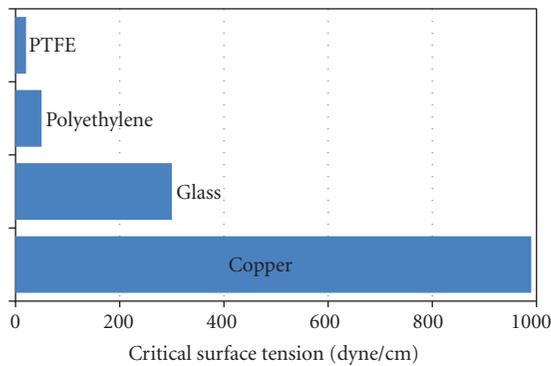


FIGURE 7: Critical surface tensions of solids (in dyne/cm).

that  $\gamma_{LA} = \gamma_{SA} - \gamma_{SL}$  or  $\gamma_{LA} \leq \gamma_{SA}$ . In other words, if the surface tension of the adhesive ( $\gamma_{LA}$ ) is less than the surface energy of the substrate surface ( $\gamma_{SA}$ ), the adhesive will spread over the substrate. For maximum adhesion, the adhesive must completely cover or spread over the substrate, that is, effectively wet it. The contact angle between the adhesive and the substrate is, therefore, a good indicator of adhesive behavior.

The value of  $\gamma_{SA}$  when  $\cos \theta = 1$  is the critical surface energy (CSE) and equals the value of  $\gamma_{SL}$  when the liquid just spreads over the surface. The critical surface tension of several materials is shown in Figure 7. The very large difference in CSE between say glass and PTFE and polyethylene indicates the difficulty of bonding to the two resins.

Wetting of the surface occurs when the adhesive surface tension ( $\gamma_{SL}$ ) is less than the critical surface energy. This is often expressed as the adhesion quotient which requires the substrate surface energy ( $\gamma_{SA}$ ) to exceed the surface tension of the adhesive liquid ( $\gamma_{SL}$ ) by 10 dyne/cm. If the reverse is true, that is, ( $\gamma_{SL} \geq \gamma_{SA}$ ), surface wetting is poor, adhesion is reduced and the adhesive tends to pull away from the surface during the curing process.

The “take home message” here is that the adhesive liquid must wet the substrate surface and such factors as surface contamination, surface conditioning, presence of moisture, and the adhesive used all affect the adhesion between substrate and adhesive. A small contact angle indicates more adhesion is present because there is an interactive force between the liquid and solid phases.

**4.2. Chemical Adhesion.** If the adhesive and substrate can form a compound at their interface or union, the ionic or covalent bonds that are formed result in a strong bond between the two materials. A weaker bond is formed when there is hydrogen bonding, that is, a hydrogen atom in one molecule is attracted to an electron-donor atom such as nitrogen or oxygen in another molecule. Thus, when the surface atoms of an adhesive and substrate form ionic, covalent, or hydrogen bonds, chemical adhesion occurs. However, it can be seen that whereas the strengths of these chemical bonds can be high, Figure 8, their lengths are short and therefore for bonding to occur, surfaces with the potential for chemical

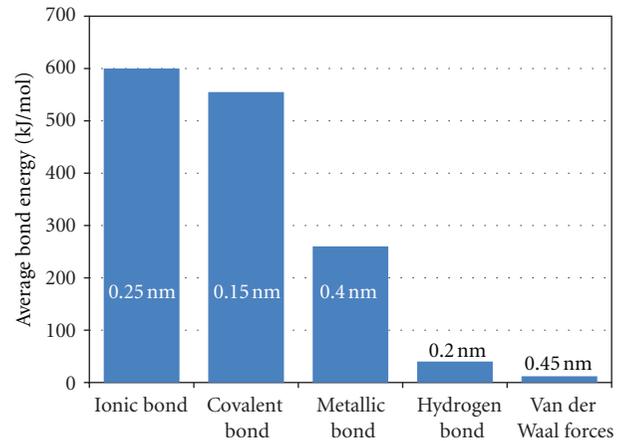


FIGURE 8: Bond energies and bond lengths of adhesive forces.

bonding must be brought very close together and remain in this proximity for the bond to be stable.

Although the average lengths of hydrogen bonds are comparable to those of covalent and ionic bonds, they are an order of magnitude weaker. In the case of dental cements, zinc polycarboxylates provide some chemical bonding between the carboxylate molecule of the cement and hydroxyapatite mineral in the tooth, whereas bonding with zinc phosphate cements is wholly mechanical in nature.

**4.3. Dispersive Adhesion.** In dispersive adhesion or physisorption, the surfaces of two materials are held together by van der Waals forces. The latter are the attractive forces between two molecules, each of which has a region of small positive and negative charge such that the molecules are polar with respect to the average charge density of the molecule; it should be noted that there may be multiple poles (regions of greater positive or negative charge) with larger and/or more complex molecules. If these positive and negative poles are an inherent property of a molecule, they are known as Keesom forces, whereas polarity, that is, a transient effect due to random electron motion within the molecules that cause a temporary concentration of electrons in one region are known as London forces. London dispersion forces, which result from statistical quantum mechanics, are particularly useful in adhesion because they arise without the need for either the adhesive or the substrate surface to have any permanent polarity. Adhesion in surface science commonly refers to dispersive adhesion.

Although van der Waals bond lengths are longer than those of other molecular forces, see Figure 8, they are still short in absolute terms so that these forces only act over very small distances. About 99% of the work required to break van der Waals bonds is performed once the joined surfaces are separated by more than a nanometer and, as a result, the effectiveness of adhesion due to chemical or dispersive bonding is limited. Once a crack is initiated, it propagates easily along the interface because of the brittle nature of the interfacial bonds and, consequently, greater contact surface areas often provide little difference in the measured adhesion.

This topic will be returned to when the adhesion zone is discussed.

**4.4. Diffusive Adhesion.** Some materials may merge or intermingle at the bonding interface by diffusion, typically when the molecules of both materials are mobile and/or soluble in each other, which typically is the case with polymer chains where one end of a molecule can diffuse into the other material. This form of interaction, known as interdigitation, occurs when a resilient denture liner is processed onto an acrylic resin denture base, or when a fractured denture is repaired with acrylic resin. In such cases, bonding arises from the mutual solubility and interactions between methyl methacrylate (monomer) in the repair (or liner) material and the surface of the poly(methyl methacrylate) or acrylic base with diffusive adhesion (bonding) resulting from sections of polymer chains from the applied material interdigitating with the substrate surface. However, the mobility of the polymers strongly influences their ability to interdigitate to achieve diffusive bonding. Cross-linked polymers are less capable of diffusion and interdigitation because of their restricted mobility whereas non-cross-linked polymers have greater mobility and interdigitate more readily. These differences account for the fact that it is easier to bond a resilient liner to a recently processed acrylic base, or even during processing of the denture base, because the acrylic resin has a greater surface reactivity, that is, there is greater mobility of its surface polymer chains, than when attempting to relin a denture base

Diffusive adhesion is also the mechanism involved in sintering as, for example, when metal or ceramic powders are compressed and heated so that atoms diffuse from one particle to the next to produce a solid mass. Diffusive bonding occurs when atoms from one surface penetrate into an adjacent surface while still being bound to their surface of origin. This is the mechanism involved in the fusing of porcelain to metal in the fabrication of a PFM crown. Since diffusive adhesion requires interaction of atomic species between two surfaces, the greater the time that the two surfaces can interact, the more diffusion occurs and, accordingly, the stronger the adhesion is between the two surfaces.

**4.5. Mechanical Adhesion.** When uncured, adhesives are fluid and they can flow over the substrate, filling the voids, rugosity, and pores of the surface and attach or “bond” to that surface by mechanical interlocking. This is often referred to as micromechanical adhesion and is shown schematically in Figure 9.

Micromechanical adhesion is the primary mechanism for luting of restorations to teeth with dental cements and probably also contributes significantly to bonding achieved with resin-based adhesives as, for example, in fissure sealants and direct bonding of restorative resins. The effectiveness of micromechanical adhesion is determined in large part by the wetting of the substrate by the luting agent in that poor wetting of the substrate by the luting agent will inhibit good apposition of cement and substrate. Further, the luting agent must be able to flow into the surface voids, and so forth, and for this process to occur, the adhesive must have a low

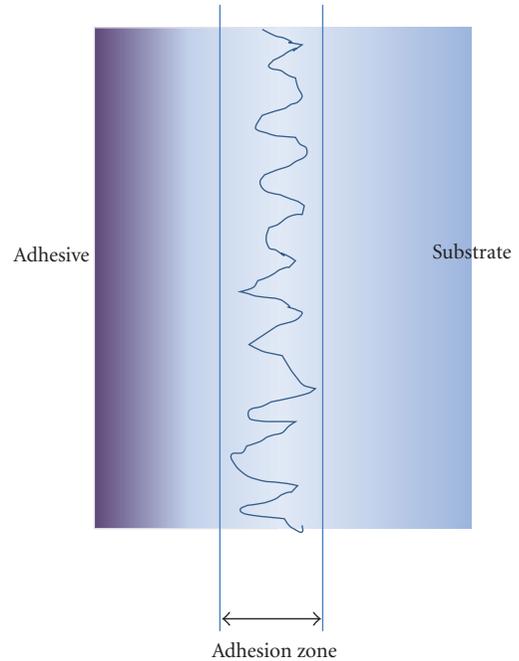


FIGURE 9: Micromechanical adhesion (schematic).

viscosity. Water, for example, has a viscosity of 1 centiPoise (cP) and that of alcohol is 1.2 cP. Many other fluids, however, have much higher viscosities, for example, 9.22 cP for eugenol (oil of cloves), 1490 cP for glycerin and  $\sim 10^4$  cP for honey, and the very large difference in the viscosities of honey and water explains why water flows far more readily than honey. It should be noted that the SI units for viscosity are Pa s (Pascal seconds) and are equivalent in magnitude to often quoted cP values.

Inevitably, micromechanical adhesion of a luting agent to a surface is not simply a matter of wetting (i.e., contact angles) and the rheological or flow properties of the adhesive. Other factors also enter into micromechanical adhesion, notably the electrostatic forces (both attractive and repulsive) that may be operating between the adhesive and the microtopography of the substrate as well as a property of the applied fluid known as thixotropy. A thixotropic fluid is one that under the action of mechanical forces such as stirring, vibration, and even kneading will temporarily transform to a state that has a lower viscosity and which exhibits better flow than the fluid in its static state. Thixotropic behavior is an important characteristic for endodontic (root canal) sealants which are required to flow into a root canal, often under vibration. Further, thixotropy is often incorporated into industrial and domestic paints by additives such as silicic acid and is probably present in various dental adhesive and cement formulations. Thixotropy, when present in an adhesive, provides certain advantages to the overall adhesion system. In particular, when a thixotropic adhesive is applied to a substrate surface, it will remain in place, even on vertical surfaces. Further, because adhesive flow is determined in part by the mechanical forces imposed on the adhesive, there can be greater control of the adhesive film thickness combined with

improved flow into the microtopography of the substrate surface.

## 5. The Adhesion Zone

It follows from the above that the adhesive bonded to a substrate often has a modified molecular structure at the bonding interface. This interfacial region is known as the adhesion zone (Figure 9) and is characterized by the changes in the adhesive (and sometimes in the substrate) that may arise from the bonding interactions.

The transition zone, the region between the bonding interface and the bulk of the adhesive, is the area over which the chemical, mechanical, and optical properties of the adhesive differ from those of the bulk adhesive. It varies in thickness, from a few nanometers up to a few millimeters, with the thickness depending on the nature of the substrate surface, the chemical composition, and physical characteristics of the adhesive being applied and the curing conditions. Where there are thick transition zones and/or narrow adhesion zones, the behavior of the entire bonding interface may be dependent on the properties of the transition zone because the properties, notably strength, of the adhesive may be impaired because of inadequate cohesion within the adhesive. It is considerations such as these that determine, at least in part, the selection of the optimum luting agent for the various combinations of luting agents and restorations that were discussed by Pameijer in his review of luting agents [8].

## 6. Adhesive Dentistry

Adhesive dentistry, whether it is the cementation (or luting) of a restoration to a prepared tooth or restoration with a composite resin, involves the application and curing of an adhesive at the interface between tooth tissue and the restorative material. Consequently, all of the aspects of adhesion and cohesion discussed above are involved in this process.

Restoration with a composite material has three principal steps. The first is the creation of microporosity in enamel or dentin by acid etching either through application of an etchant or by the *in situ* action of an etchant/primer/adhesive. The second step is the application of a primer/adhesive which wets and penetrates the created microstructure although because the surface energies of etched enamel and etched dentin differ, different primers are required for the two substrates. Finally, a resin is applied to the primed surface so that when polymerized *in situ*, it micromechanically (i.e., there is mechanical adhesion) interlocks with the substrate microporosity together with a degree of chemical bonding, with some materials exhibiting better chemical adhesion than others.

## 7. Dentin Bonding

Bonding to dentin presents greater problems than to enamel because it has a high organic content, a non-uniform composition and it is permeated by tubules. Further, after mechanical treatment, a 3–15  $\mu\text{m}$  thick, featureless, and poorly adhe-

rent smear layer of organic debris will form. While this smear layer can provide pulpal protection by reducing dentin permeability, it hinders bonding.

Bonding to dentin involves three stages, namely, conditioning, priming, and bonding, although some commercial bonding systems combine two or more stages into a single step. The conditioning stage involves modifying or removing the smear layer by acidic conditioners, the precise approach being determined by the bonding system used. Priming is the key step in dentin bonding because it promotes interactions between hydrophobic restorative resins and hydrophilic dentin. Primers (dentin bonding agents) are bifunctional molecules, one end being a methacrylate group that bonds to resin and the other a reactive group that reacts with dentin. Thus, primers are coupling agents, that is, they are bifunctional molecules that primarily bond to calcium but may also interact with collagen. The bonding (adhesive) agent is a fluid resin that flows over and wets the primed surface to form an effective bond when cured *in situ*.

It should be noted that many manufacturers combine many of the conditioning, priming and bonding steps in their systems. If the primer and conditioner are combined as with self-etching primers, the smear layer is incorporated within the primer that directly contacts the dentin and constitutes the adhesive zone. The subsequently applied restorative resin bonds to primed dentin when polymerized. An advantage with self-etching primers is that the dentin is maintained in a moist condition throughout the bonding procedure although enamel etching with such systems is less effective than with phosphoric acid treatment. Alternatively, the primer and adhesive may be combined so that the applied material will infiltrate the collagenous network created by conditioning to form a hybrid (resin-infiltrated reinforced) layer. Subsequently, applied restorative resin, when polymerized, bonds everything together.

Although high bond strengths ( $\geq 20$  MPa) to dentin may be achieved, bond failures commonly involve cohesive fracture of the dentin such that these systems are not infallible. They tend to be technique and material sensitive and may require successive treatments for optimal bonding. Further, regardless of high bond strengths, which suggest good adaptation to the dentin, good bonding and the absence of leakage are not synonymous and no system provides consistent leak-free restorations.

## 8. Conclusions

It follows from the above discussion that the performance of an adhesive in the luting of a restoration to a tooth will be dictated by a multiplicity of factors. Ideally, laboratory bond strength test values and the resistance of luted restorations to clinical loads will be maximized when the propagating crack that causes bond failure has to travel through the adhesion zone rather than the bulk adhesive. In other words, optimal retention is achieved when adhesion rather than the cohesive strength of the adhesive determines the overall strength of the bond [9]. Nevertheless, the mechanical

properties of the luting agent often can have a marked impact on the resistance of the luted restoration to applied forces when the thickness of the cement film is markedly greater than the width of the adhesion zone, as noted by *in vivo* determinations of cement film thicknesses beneath restorations [10].

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## Research Article

# Waiting Time for Coronal Preparation and the Influence of Different Cements on Tensile Strength of Metal Posts

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This study aimed to assess the effect of post-cementation waiting time for core preparation of cemented cast posts and cores had on retention in the root canal, using two different luting materials. Sixty extracted human canines were sectioned 16 mm from the root apex. After cast nickel-chromium metal posts and cores were fabricated and luted with zinc phosphate (ZP) cement or resin cement (RC), the specimens were divided into 3 groups ( $n = 10$ ) according to the waiting time for core preparation: no preparation (control), 15 minutes, or 1 week after the core cementation. At the appropriate time, the specimens were subjected to a tensile load test (0.5 mm/min) until failure. Two-way ANOVA (time versus cement) and the Tukey tests ( $P < 0.05$ ) showed significantly higher ( $P < 0.05$ ) tensile strength values for the ZP cement groups than for the RC groups. Core preparation and post-cementation waiting time for core recontouring did not influence the retention strength. ZP was the best material for intraradicular metal post cementation.

## 1. Introduction

The cast metal core is a component frequently used to restore endodontically treated teeth with extensive coronal destruction [1, 2]. Post retention in the root canal is fundamental for the longevity and success of treatment. Length, shape, diameter, and post surface, as well as the type of cement used, are factors that may affect core retention and stability. A prefabricated retainer must adapt adequately to the prepared root canal; otherwise, a cast post and core should be the treatment option [3].

There is no consensus with regard to the choice of a luting agent for cast metal cores; therefore, the choice of cement must take into consideration its biological and functional properties [4, 5]. An ideal luting agent must be sufficiently fluid to flow, provide adequate working and setting time to allow the part to seat, permit easy removal of excess material, and allow adjustments to be made to the part without losing retention. Cements can retain the core in the root canal mechanically, chemically, or by other means. Mechanical

bonding is not always effective for retention, and a cement with the potential to chemically bond to tooth surfaces and prosthesis may be indicated [6].

In addition to being the material most frequently used for this purpose, zinc phosphate cement is the oldest of the luting agents; therefore, it serves as a standard for comparison with new systems [7–9]. It does not bond chemically but bonds only by mechanical interlocking at the interfaces. It has high resistance and forms a thin film; it can support elastic deformations even when it is used as a luting agent for restorations subject to high masticatory stresses [10].

More recently, resin cements have become an alternative to zinc phosphate cement, particularly because they are practically insoluble in the oral medium and have adhesive properties [1, 9, 11, 12]. Dual-activated cements provide long working time until they are exposed to light activation, and, due to the chemical polymerization process, their bond strength continues to increase over time [13]. However, after posts have been cemented with resin agents, stresses produced by polymerization shrinkage may harm the integrity

of the bond between the resin cement and the root canal walls [1]. The use of sodium hypochlorite as an irrigant solution during endodontic treatment, as well as filling cements containing eugenol in their formulae, may also influence retention of posts cemented with resin cement [14–16]. Some studies have concluded that cores cemented with zinc phosphate cement have retention values higher than or similar to those cemented with resin cements [17–20]. However, other studies have shown better performance of resin cements when compared with zinc phosphate cement [21].

Amongst the various reasons for failure in teeth restored with a core, detachment, displacement, and root fracture occur more frequently [22]. Occlusal forces and predominantly functional and occasionally parafunctional forces tend to make cemented posts unstable in teeth that need coronal reconstruction [9].

Coronal preparation of the cast metal core after cementation may contribute to reducing its retention. Studies have proved the capacity of ultrasound vibration in facilitating removal of cemented posts in endodontically treated teeth [21, 23]. High-speed rotary instruments cause similar vibrations, which suggests that the layer of cement formed between the tooth and post may be fractured, thus compromising core retention [24].

The aim of this study was to investigate the effect of post-cementation waiting time for coronal preparation of core and the different types of cement had on cast metal core retention in root canals.

## 2. Methods and Materials

In this study, 60 extracted human canines of approximately the same size were collected and stored in aqueous 0.1% thymol. Each tooth was sectioned perpendicularly to its long axis 16 mm from the root apex, using a double-faced diamond disk number 7020 (KG Sorensen Ind. e Com. Ltda, Barueri, SP, Brazil) coupled to a straight handpiece at low speed, leaving a flat surface. The largest vestibular-lingual (VL) and mesiodistal (MD) diameters of the flat surfaces of the roots were recorded with a digital pachymeter (Mitutoyo Sul América LTDA., Suzano, SP, Brazil). These measurements were statistically compared to certify that the difference between the areas was not significant, and the discrepant teeth were eliminated.

The root canals were debrided conventionally with the K-type files up to number 45 (Maillefer Instruments, Ballaigues, Switzerland), irrigated with 5 mL of 2.5% sodium hypochlorite over 5 minutes, and filled using the lateral condensation technique with gutta-percha and a calcium hydroxide-based and eugenol-free endodontic cement (Sealer 26, Dentsply Materiais Odontológicos, Rio de Janeiro, RJ, Brazil). The teeth were sealed with temporary cement (Coltosol, Vigodent SA Ind. e Com., Rio de Janeiro, RJ, Brazil) and stored in distilled water in an oven at 37°C for 7 days.

To prepare the cores, 10 mm of root filling was removed with a Peeso bur (number 4 Maillefer Instruments, Ballaigues, Switzerland) at low speed controlled with a cursor. The root canals were cylindrical with 10 mm length and

1,3 mm diameter; they had the Peeso bur number 4 dimensions. To complete the preparation, a small channel was made on the internal vestibular wall of the root canal with a spherical carbide bur number 4 (KG Sorensen Ind. e Com. Ltda, Barueri, SP, Brazil) to guide the insertion of the cast core and prevent it from rotating.

The root canals and coronal surfaces were isolated with lubricant gel (KY, Johnson & Johnson Industrial Ltda, São José dos Campos, SP, Brazil) to mold the cores. Patterns were made of acrylic resin (Duralay, Reliance Dental Mfg. Co., USA) with the aid of prefabricated plastic posts (PinJet, Angelus, Londrina, PR, Brazil) for use in the 60 prepared teeth. In order to standardize the coronal portion of the cores, hollow crowns were used (Provjet-Angelus-Londrina, Paraná, Brazil). All the cores were made 1 mm short from the external margin of the flat coronal face of the tooth. The cores were cast in Ni-Cr alloy (Talladium do Brasil, Curitiba, PR, Brazil) and tested in the respective root canals to verify adaptation and were then subjected to airborne abrasion with 50 µm aluminum oxide particles. A diamond tip was used to make scratches on the external root surface, perpendicular to the long axis, to provide additional retention of the root during tensile testing.

Each tooth was fixed on the rod of a delineator (Bio Art, Art Equipamentos Ltda, São Carlos, SP, Brazil) with the aid of a number 4 Peeso reamer (Maillefer Instruments, Ballaigues, Switzerland) fitted to the canal so that the roots were perpendicular to the ground. They were then embedded in resin blocks. Proper devices were developed for the embedded specimens so that they would fit into the adaptor of the universal testing machine.

The teeth were cleaned with detergent (Tergensol, Inodon Laboratório, Porto Alegre, RS, Brazil) and the cast metal cores were also washed with detergent (Limpol, Bombril S/A, Abreu e Lima, PE, Brazil). The teeth were randomly divided into 2 cement groups ( $n = 30$ ). The cast metal cores in the first group were cemented with zinc phosphate cement (SS WHITE Artigos Dentários Ltda, Rio de Janeiro, RJ, Brazil) using the technique described in Table 1, and in the second group they were cemented with resin cement (Panavia F, Kuraray Co., Osaka, Japan). The latter group was used in accordance with the manufacturer's recommendations. Table 1 describes the characteristics of the cements used and the manufacturers' instructions. The resin cement was placed only on the post. The zinc phosphate cement was placed on the post and also inserted into the canal with the aid of a Lentulo spiral (Maillefer Instruments, Ballaigues, Switzerland). After cementation, all the specimens were placed in a manual press and submitted to a 5 kgf pressure for 10 minutes to assure complete adaptation of the cast metal cores in the respective roots. The excess zinc phosphate cement was removed immediately after setting (10 minutes). In order to remove the excess resin cement, it was light activated for 10 seconds on the incisal margin of the core in the direction of the root. Each face of the tooth was then light activated for another 20 seconds with the light facing the core-tooth interface. To light activate the resin cement, a halogen light-curing appliance (Optilight LD MAX, Gnatus, Ribeirão Preto, SP, Brazil) with an irradiance of 450 mW/cm<sup>2</sup>

TABLE 1: Characteristics of the cements used and the manufacturers' instructions.

Cement batch number manufacturer	Composition	Manufacturer's instructions
Zinc Cement Powder-0711008 Liquid-0010308 SS WHITE Artigos Dentários Ltda-RJ	Powder-zinc oxide, magnesium oxide, coloring agents Liquid-phosphoric acid, aluminum hydroxide, zinc oxide, distilled water	Recommended proportion: a small scoop measure of powder to 4 drops of liquid. Place powder on glass plate and divide it into multiple small parts. Shake the flask of liquid and drip liquid onto the plate. Begin mixing the powder and liquid immediately for 10 seconds per part, using a wide area of the plate. The powder was included incrementally to avoid excess heat development. Adequate consistency for cementation will be obtained when the mixture is creamy and leaves the spatula forming a sticky drop over a period of 60 to 90 seconds.
Panavia F 51203 Kuraray Co., Osaka, Japan	Paste A—10 methacryloyloxydecyl-hydrogen phosphate, hydrophobic and hydrophilic dimethacrylate, benzoyl peroxide, camphorquinone, colloidal silica Paste B—sodium fluoride, hydrophobic and hydrophilic dimethacrylate, diethanol- <i>p</i> -toluidine, Isopropyl T-sulphonate sodium benzoate, barium glass, titanium dioxide, colloidal silica	Tooth Preparation: mix 1 drop each of liquid A and B of ED Primer. Using a microbrush, apply the mixture in the root canal and wait 60 seconds. Remove excess primer with paper cone and conclude drying with light air jet. Paste Preparation: dispense equal quantities of pastes A and B on the manipulation block. The minimum quantity of paste should correspond to a half turn of the syringe. Mix the pastes for 20 seconds. Apply the paste to the post and on the coronal remainder. Insert the post into the canal and polymerize for 20 seconds.

TABLE 2: Tensile strength means in Kgf (standard deviations) between the groups and study times.

Times	Cement	
	Zinc phosphate	Resin cement
Control	31.65 ( $\pm$ 12.10) Aa	8.65 ( $\pm$ 3.08) Ba
15 minutes	33.26 ( $\pm$ 10.44) Aa	8.48 ( $\pm$ 4.71) Ba
7 days	27.21 ( $\pm$ 6.50) Aa	7.48 ( $\pm$ 4.33) Ba

Means followed by different letters (capitals letters in the lines and lower case letters in the columns) differ among themselves by the Tukey test ( $P < 0.05$ ).

was used. Each group of 30 teeth was subdivided into the following three groups ( $n = 10$ ): Group 1 (control), time delay after setting; Group 2, coronal portion of post space prepared 15 minutes after cementation; and Group 3, coronal portion of post space prepared 7 days after cementation. The teeth were stored in a 100% humidity environment heated to 37°C during the storage time. Figure 1 shows a diagram illustration presenting the experimental design of the tensile strength test.

The test specimens were fixed to a lathe and the metal cores were prepared by the same operator, using a tapered round trunk diamond tip (number 2135, KG Sorensen Ind. e Com. Ltda, Barueri, SP, Brazil) at high speed under cooling. The diamond tip was changed after every three preparations.

The coronal portion of the cores was prepared for 4 minutes: 3 minutes of axial preparation and 1 minute of incisal preparation. For the axial preparation, the diamond tip was placed so that it touched only the core in the direction of the long axis of the tooth, simulating preparation for a metal-ceramic crown. The diamond tip remained in contact with the core and the operator sought to exert constant

pressure, going over all the faces of the core. For the incisal preparation, the diamond tip was placed forming an angle of 45° with the base.

All the test specimens were submitted to the tensile test 7 days after cementation. Tensile strength tests were performed in a testing machine (EMIC, São José dos Pinhais, PR, Brazil) at speed of 0.5 mm/min with a load cell of 2000 Kgf. The samples were placed and fastened to an adaptor at the base of the machine. A device on the active part of the machine was placed on the coronal portion of the cast metal core so that tensile force would be applied in the direction of the long axis of the tooth. As soon as the core was displaced, the test was interrupted and the displacement force value was recorded in the program. The tensile strength values were obtained in Kgf.

### 3. Results

Table 2 shows the results of the tensile strength test (mean and standard deviation) and the results of the Tukey test. The tensile strength values of the samples cemented with zinc phosphate cement were statistically higher than those of the samples cemented with Panavia F resin cement. None of the samples in either group were influenced by the post-cementation time interval waiting for coronal preparation of the core.

### 4. Discussion

Intraradicular posts are widely used to restore endodontically treated teeth that have insufficient coronal tooth structure to retain a definitive restoration [25, 26]. The use of prefabricated posts has become commonplace due to the satisfactory

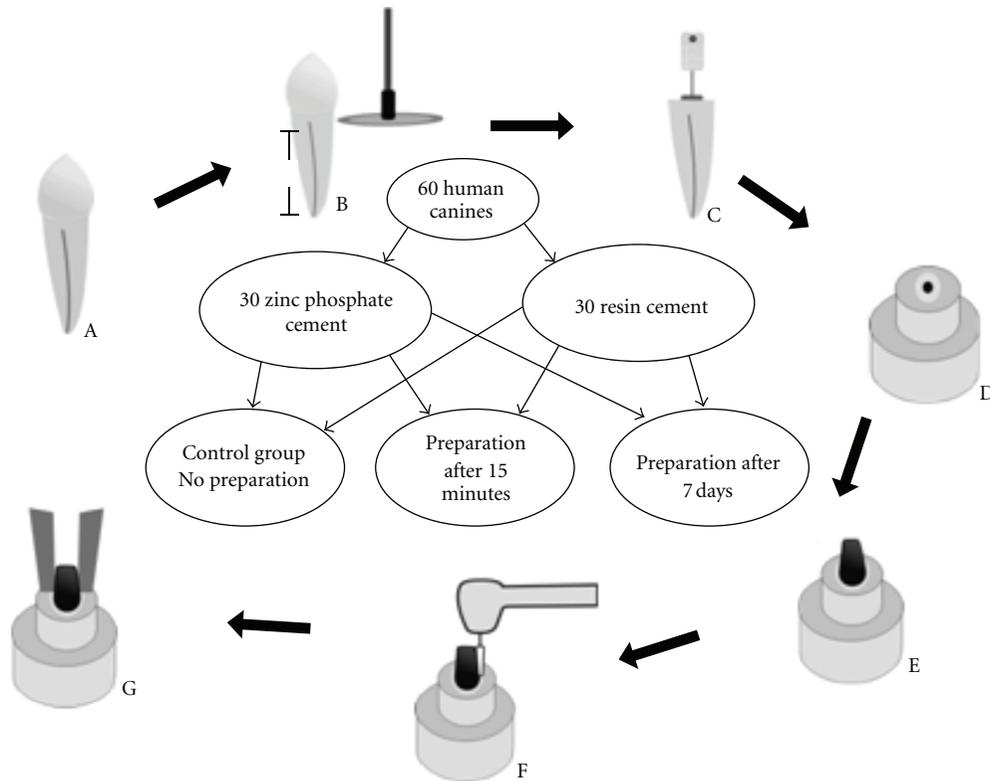


FIGURE 1: (A) Recently extracted canine. (B) Section of tooth. (C) Endodontic treatment. (D) Embedded sample. (E) Cemented cast metal core. (F) Coronal preparation of core. (G) Tensile test.

results, the reduction in clinical attendance time, and its quick application, which allows enhanced preservation of the tooth structure. However, a prefabricated retainer must adequately adapt to the prepared root canal; otherwise a cast post and core may be the treatment option [3].

Traditionally, zinc phosphate cement has been used to cement intraradicular retainers, although they have the disadvantage of lacking a bond both to the retainer and to the tooth structure [27]. In this regard, the retention provided by zinc phosphate is based mainly on mechanical interlocking. In addition to showing good results in retention tests, zinc phosphate cement has shown satisfactory performance in flexural tests and resistance to rotational forces [3, 6, 8, 10, 24]. On the other hand, resin cements have also been indicated for cementation of intraradicular retainers [6]. This type of cement could favor the retention of cast metal cores and prefabricated posts. Using resin cements was suggested mainly to strengthen the remainder of the tooth, due to the advancement of adhesive systems with properties of bonding to metals [18, 19, 23].

When comparing the means obtained by the resin luting agent and zinc phosphate cement in this experiment, it was observed that the latter showed better performance, corroborating other studies that also showed better results for zinc phosphate in comparison with resin composite used as luting agent in cast metal posts [9, 17, 20]. The hardening of zinc phosphate cement does not involve any reaction with the surrounding mineralized tissue or other restorative

materials. Therefore, the main bond occurs by mechanical interlocking at the interfaces and not by chemical interactions. Due to this method of bonding, it may be inferred that the original adaptation of retainers before cementation and their irregularities may increase the retention of metal cores cemented with zinc phosphate cement.

Perfect adaptation of cast metal cores to the prepared canal results from the formation of a very thin film of cement. Zinc phosphate cement forms a thinner film than the resin cement, which may have contributed to the former's better performance observed in the present study. Due to frictional mechanical retention of the parts involved [6, 9], fracture of this thin film is made more difficult when there is a demand by traction.

The technique used to cement prosthetic parts may influence their final retention. The manufacturer of Panavia F does not recommend inserting the cement into the root canal with the aid of a Lentulo spiral because the cement setting may be altered due to the movement of particles, accelerating its setting time. This occurs due to the mixture of cement with the catalyzer (Ed Primer). However, the use of a Lentulo spiral to take the cement into the root canal when cementing cast posts, in addition to the cement applied on the post, prevents the presence of empty spaces inside the canal [8]. In this study, this technique was used for zinc phosphate cement, but not resin cement, which may have contributed to the more favorable result of the former than that obtained with the latter.

On the other hand, sodium hypochlorite, traditionally used as a chemical irrigant in endodontic treatment, may remove organic components from dentin, especially collagen, influencing the resin cement bonds to dentin. This might increase penetration of monomers into the demineralized dentinal structure; however, sodium hypochlorite dissociates into sodium chloride and oxygen. The oxygen present at the tooth-resin cement interface could inhibit cement polymerization and interfere in resin penetration into the dentinal tubules [14, 15]. In this regard, the use of sodium hypochlorite as an irrigant of canals may also have lowered the mean bond strength of the resin cement.

Another factor relative to endodontic treatment that might interfere with polymerization and resin cement bonding is the use of filling cements containing eugenol in their composition [16]. In order to avoid this interference, calcium hydroxide-based and eugenol-free filling cement was used.

The importance of adhesive systems in contemporary dentistry is unquestionable [1, 3, 6, 9]. The introduction of resin cements in dentistry has provided a significant improvement in the success rates of restorations retained by intraradicular retainers [12]. Thus, the good performance of resin cements in comparison with zinc phosphate cement has also been reported in the cementation of cast metal cores, prefabricated posts, indirect restorations, and fixed dentures [3, 5, 6, 21, 25, 28]. There are studies that have compared the retention of cast titanium cores cemented with zinc phosphate cement and resin cement and found no difference between the two types of cements [18, 19]. It should be pointed out that resin cements have some disadvantages; such as it is critical to use the correct technique, it is difficult to remove excess material when cementing, and it has a high cost [6].

Some studies have suggested that the lower values shown by resin cements in comparison with zinc phosphate cement are due to stress generated during polymerization shrinkage of resin cement, which causes its displacement from the dentinal surface as well as incomplete bonding. The high cavity factor (i.e., C factor) of a root canal and the impossibility of light from the light-curing unit penetrating deep enough into the canal may interfere and lead to the low tensile strength values [1, 15]. The use of a primer containing coinitiators, such as Panavia F ED Primer, is essential for the polymerization of resin cement when it is not exposed to light activation. Despite the capacity of the acid resin monomer present in Panavia F ED Primer to produce bonding between the resin composites and metal, the bond strength shown by Panavia F was not higher than the one shown by the zinc phosphate cement.

Some studies indicate that immature cement that is disturbed during setting time due to the preparation of the core may cause loss of cementation and, consequently, displacement of the post and it is suggested that the use of high-speed rotary instruments during the core reparation is capable of causing vibration [26], damaging the cement film between the post and the root canal surface. Therefore, it is recommended that this type of preparation should not be performed immediately after cementation of intraradicular

retainers [24, 29]. However, this study showed that the preparation of metal cores had no influence on the retention values obtained by tensile test. The differences in the results of these studies can be attributed to the variations in the study model that affect their clinical performance [24], particularly with regard to resin cements, technique sensitivity, and the difficulties with manipulation.

One of the relevant physical properties of the cement for retaining fixed dentures is its mechanical properties. Although zinc phosphate cement shows relatively low solubility in water, it is very resistant and capable of supporting elastic deformations even when it is used as a luting agent for restorations subject to high masticatory stresses [27].

In this study, the retention values of the zinc phosphate cement were much higher than those for the resin cement. There are some factors that may justify the results found, such as the methods of inserting the cement into the root canals, difficulty of polymerizing resin cement, cement film thickness, and the use of sodium hypochlorite to irrigate the root canals. Zinc phosphate cement is less sensitive to technique and is more retentive in the cementation of cast metal cores than resin cement and, therefore, it is recommended over resin cement. Coronal preparation of the core performed immediately after cementation did not diminish its retention, which favors the use of this clinical procedure due to its reduction in working time.

## 5. Conclusion

It may be concluded that cast metal cores cemented with zinc phosphate cement showed higher tensile strength values in comparison with resin cement. The preparation time of metal cores did not influence retention values obtained by the tensile test.

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## Research Article

# Quantitative Evaluation by Glucose Diffusion of Microleakage in Aged Calcium Silicate-Based Open-Sandwich Restorations

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This study compared the *in vitro* marginal integrity of open-sandwich restorations based on aged calcium silicate cement versus resin-modified glass ionomer cement. Class II cavities were prepared on 30 extracted human third molars. These teeth were randomly assigned to two groups ( $n = 10$ ) to compare a new hydraulic calcium silicate cement designed for restorative dentistry (Biodentine, Septodont, Saint Maur des Fossés, France) with a resin-modified glass ionomer cement (Ionolux, Voco, Cuxhaven, Germany) in open-sandwich restorations covered with a light-cured composite. Positive ( $n = 5$ ) and negative ( $n = 5$ ) controls were included. The teeth simultaneously underwent thermocycling and mechanocycling using a fatigue cycling machine (1,440 cycles, 5–55°C; 86,400 cycles, 50 N/cm<sup>2</sup>). The specimens were then stored in phosphate-buffered saline to simulate aging. After 1 year, the teeth were submitted to glucose diffusion, and the resulting data were analyzed with a nonparametric Mann-Whitney test. The Biodentine group and the Ionolux group presented glucose concentrations of  $0.074 \pm 0.035$  g/L and  $0.080 \pm 0.032$  g/L, respectively. No statistically significant differences were detected between the two groups. Therefore, the calcium silicate-based material performs as well as the resin-modified glass ionomer cement in open-sandwich restorations.

## 1. Introduction

Calcium silicate cements, such as the Portland cement, possess good mechanical properties but are not commonly used in medicine because their long setting times render them unsuitable for clinical applications; maximum compressive strength is achieved after 28 days [1]. In addition, they contain heavy metals [2], are not radiopaque [3], and have a large setting expansion [4]. Nevertheless, efforts have been made to overcome these problems, and several calcium silicate-based cements have recently been introduced in medicine and dentistry. In medicine, calcium silicates are mainly used as bone graft materials [5–7]. In dentistry, they have been tested for treatment of dentin hypersensitivity [8] and gave promising results in endodontics [9]. However, the most famous calcium silicate cement remains the mineral trioxide aggregate (MTA; Dentsply, Tulsa Dental Specialties, Johnson

City, Ten, USA). MTA was introduced in 1993 [10] and is designed for root-perforation treatment, retrograde filling, and open-apex closure on immature teeth. Three excellent reviews have described the physical and bacteriological properties [11], the leakage and biocompatibility investigations [12], and the mechanisms of action [13] of MTA.

The Portland cements designed for medicine and dentistry, also called hydraulic silicate cements [14], mainly contain tricalcium silicate ( $3\text{CaO}\cdot\text{SiO}_2$ ;  $\text{C}_3\text{S}$ ), because it is responsible for rapid setting and development of early strength and exhibits higher reactivity than the other calcium silicates [15]. Unfortunately the  $\text{C}_3\text{S}$ -based materials that combine a fast setting time with outstanding biological properties have poor mechanical properties that make them inappropriate for restorative dentistry [16–18]. More recently, a fast-setting calcium silicate-based restorative material especially designed for restorative dentistry has been brought onto

the market (Biodentine, Septodont, St Maure des Fossés, France). This material exhibits the same excellent biological properties as MTA and can be placed in direct contact with dental pulp [19], although its sensitivity to abrasion makes it a poor enamel substitute. However, Biodentine may be a good candidate for a dentin substitute in sandwich restorations: it does not require photoactivation and thus can be placed in bulk in the cavity, its setting time is short enough to complete the whole procedure in a single appointment, its mechanical properties are sufficient to withstand occlusal loading when protected with composite.

Leakage at the dentin material interface is responsible for postoperative sensitivity [20] and secondary caries [21]. Therefore, leakage of Biodentine which belongs to a new class of restorative material must be evaluated. It should preferably be compared with the resin-modified glass ionomer cements which have been utilized previously as a base material for this type of restoration in both laboratory and clinical investigations, with some degree of success [22]. To our knowledge, calcium silicate cements are not frequently used in restorative dentistry and their marginal integrity when used in open-sandwich restorations has never been tested. The purpose of this study was to compare the *in vitro* marginal integrity of open-sandwich restorations based on aged calcium-silicate cement versus resin-modified glass ionomer cement.

## 2. Materials and Methods

Thirty human third molars extracted due to dental crowding were used for this study. The teeth were collected and all remnants of soft tissue were immediately removed with gauze. The teeth were stored in 0.5% Chloramine-T at 4°C until usage within 2 months of collection. These experiments were performed according to national ethical laws. Only sound fully formed teeth lacking any sign of cracking due to the use of forceps were included in the study.

**2.1. Specimen Preparation.** After visual inspection with a light microscope to ensure that the teeth did not present caries or cracks due to extraction, the teeth were cleaned and polished with scalers and pumice. One standardized mesio-occlusal class II cavity was prepared on each tooth. All manipulations and restorations were performed by a single experienced operator to prevent variation due to operator skill. The operator performed these procedures under 3.5x magnification with fiber optic headlight illumination. Cavities were prepared with a high-speed handpiece, using a diamond bur (ISO 6856310023, Komet, Lemgo, Germany) under heavy water spray. The diamond bur was replaced after every five preparations. All internal line angles were rounded. The overall dimensions and depths of cavities were standardized as follows: occlusal floor, width 4 mm, length 5 mm; axial wall, width 4 mm, height 3 mm; gingival floor, width 4 mm, depth 2.5 mm. The proximal boxes ended in dentin, just below the enamel-cementum junction. The teeth were immediately and randomly divided into two groups according to the filling material used for the sandwich restoration: the Biodentine-group teeth ( $n = 10$ ) were filled with calcium silicate-based Biodentine; the Ionolux-group teeth ( $n = 10$ )

were filled with the resin-modified glass ionomer cement Ionolux. The negative control teeth ( $n = 5$ ) were prepared and filled as in the Biodentine group but were entirely covered with two layers of nail varnish, and the positive control teeth ( $n = 5$ ) were completely filled with TetricEvo Ceram (Ivoclar Vivadent, Schaan, Liechtenstein) without dentin wall treatment and without dentin-bonding agent between the dentin walls and the restorative material.

### 2.2. Cavity Filling

**Biodentine Group.** An Automatrix (Dentsply, Konstanz, Germany) was adjusted around the cavity and secured. The cavity was filled with Biodentine (Table 1) prepared according to the manufacturer's recommendations. After a 48 hours setting at 37°C and 100% humidity, a diamond bur mounted on a high-speed handpiece under copious water coolant was used to remove all material, leaving only the cervical third of the Biodentine filling on the gingival floor. The cavity was totally etched with 32% orthophosphoric acid for 15 s and thoroughly rinsed, and the enamel margins were etched for an additional 15 s and rinsed. The dentin walls were treated with All Bond 2 (Bisco, Schaumburg, Ill, USA) and the cavity was filled with three increments of TetricEvo Ceram composite. Each increment was light cured for 3 s, according to the soft polymerization concept, and finally cured for 40 sec. Composite was applied with a special instrument (CVHL1/2, Hu Friedy, Chicago, Ill, USA). The fiber optic headlight was turned off during the filling procedures to prevent premature partial polymerization of the light-curing material. The dentin-bonding agent and the composite were polymerized with a Blue phase 20i (Ivoclar-Vivadent) using a new 11-mm tip. The curing light was tested before each restoration and measured at least 1600 mW/cm<sup>2</sup> each time on a curing radiometer (Demetron, Bioggio, Switzerland).

**Ionolux Group.** The smear layer covering the dentin walls was removed using 10% polyacrylic acid for 20 s. After rinsing for 20 s, an Automatrix was adjusted and secured. The resin-modified glass ionomer cement (Ionolux; Voco, Cuxhaven, Germany) was prepared according to the manufacturer's recommendations and placed in bulk to fill the cervical two-thirds of the cavity. The Ionolux was allowed to chemically set for 5 min and then was light-cured for 40 s; light curing did not occur immediately to permit material spreading and setting stress relaxation. The teeth were then prepared as described for the Biodentine group; cavity preparation leaving the cervical third filled with Ionolux, total etching, dentin bonding agent application, and cavity filling with TetricEvo Ceram.

**2.3. Thermo-Mechanocycling.** The teeth simultaneously underwent thermocycling and mechanocycling using a fatigue cycling machine (Proto-tech, Portland, Ore, USA) in conjunction with two recirculating water baths, a refrigerated bath (Merlin 33, Thermo Neslab, New Ington, NH, USA), and a heating bath (Isotemp 3016H, Fisher Scientific, Pittsburg, Pa, USA) [22]. A peristaltic water pump was used to return water from the teeth to the baths. These four devices

TABLE 1: Chemical composition of Biodentine, Septodont, St Maure des Fossés, France.

(i) Tricalcium silicate ( $\text{CaO}$ ) <sub>3</sub> $\text{SiO}_2$
(ii) Calcium carbonate: $\text{CaCO}_3$
(iii) Zirconium dioxide: $\text{ZrO}_2$
Liquid:
(i) Calcium chloride: $\text{CaCl}_2$
(ii) Water
(iii) Water reducing agent

were connected to three 3-way solenoid valves permitting adequate liquid circulation. Bath temperatures were self-regulated; the dwell time and the mechanical parameters were under control of the fatigue cycling machine. The dwell time was set at 30 s for 12 hours (720 complete cycles), and the bath temperatures were set at 5°C and 55°C. The teeth were mounted into acrylic potting rings, and the roots were partly embedded in epoxy resin (Buehler, Lake Bluff, Ill, USA) to secure the teeth. A guide rod, representing the stylus of the fatigue cyler, was used to adjust the specimen position so that the guide rod touched the restoration exactly where the round-ended stylus was placed during mechanocycling (in the center of the occlusal composite restoration). The acrylic rings containing the teeth were placed 5 by 5 in the mechanocycling device and secured for a 12-h thermo-mechanocycling. The loading device delivered an intermittent axial force of 50 N at 2 Hz for a total of 86,400 cycles.

**2.4. Aging.** Each group of teeth was stored for 1 year at 4°C in Dulbecco's phosphate-buffered saline with 0.5% chloramine-T added to prevent bacterial contamination (Table 2). The vials were frequently mixed and the liquid was renewed every 2 months. Aging was included to permit potential proximal dissolution of the dentin substitute.

**2.5. Glucose Diffusion.** The teeth were placed upside down in a plate and the pulp cavity was filled, through the open apices, with 60  $\mu\text{L}$  of bi-distilled water plus 0.2%  $\text{NaN}_3$ . The plates were filled with 1 M glucose plus 0.2%  $\text{NaN}_3$  solution in water added such that the cavity margins were below the glucose solution level, but the apices were higher than the glucose solution level (Figure 1). The teeth were left in the plates for 1 h, allowing glucose diffusion from the glucose solution toward the pulpal space filled with bi-distilled water. Forty microliters of this liquid were collected from each tooth and placed in a 96-well plate. The preceding steps were all performed using high-magnification binoculars. The glucose concentration was determined with a glucose assay kit (Sigma Chemicals, St Louis, Mo, USA) according to the manufacturer's recommendations and recorded using a spectrophotometer at 540 nm. The results were expressed in g/L using a standard curve established prior to experimentation, from 0 to 100  $\mu\text{g}/\text{mL}$  (Figure 2). Since the sample size was less than 30, a nonparametric Mann-Whitney test was performed, at the 95% confidence level, to compare the groups.

TABLE 2: Composition (in g/L) of the Dulbecco's phosphate buffered saline used for the study.

(i) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ :	0.133
(ii) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ :	0.1
(iii) KCl:	0.2
(iv) $\text{KH}_2\text{PO}_4$ :	0.2
(v) NaCl:	8.0
(vi) $\text{Na}_2\text{HPO}_4$ :	1.15

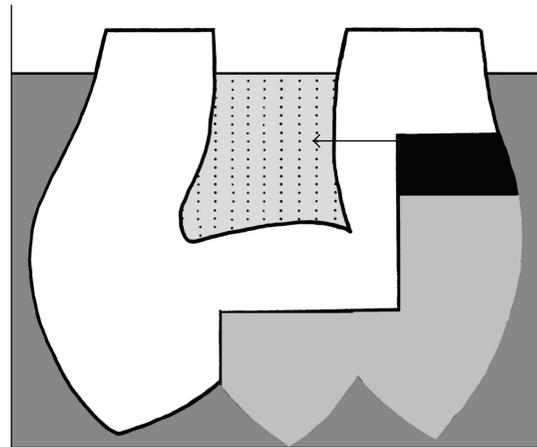


FIGURE 1: The glucose diffusion test. The tooth, with the lining material (in black) and the composite (in grey), was placed upside-down in 1 M glucose (dark grey), with the level of the solution below the tooth apex. Glucose diffused through the dentin-material interface and reached the pulpal space filled with water (dotted grey). The diffusion pathway is depicted by the arrow.

### 3. Results

**3.1. Glucose Diffusion.** The Mann-Whitney showed a statistically significant difference among the two groups and the two controls ( $P < 0.001$ ). The negative controls were statistically different from both material groups which were in turn different from the positive controls. The negative controls were below the detection limit of the glucose test and positive-control glucose diffusion was measured as  $0.450 \pm 0.320$  g/L (Table 3). Glucose concentrations of  $0.074 \pm 0.035$  g/L and  $0.080 \pm 0.032$  g/L were recorded for the Biodentine group and the Ionolux group, respectively. The test failed to detect a statistically significant difference between both cements; the two materials thus allowed similar glucose diffusion at the interface between the restorative materials and the dentin walls.

### 4. Discussion

This study compared the *in vitro* marginal integrity of open-sandwich restorations based on aged calcium silicate-cement or resin-modified glass ionomer and concluded that no statistically significant difference exists between the two treatments. The new calcium silicate-based material performed as well as the resin-modified glass ionomer cement. In addition, the calcium silicate cement did not require specific preparation of the dentin walls.

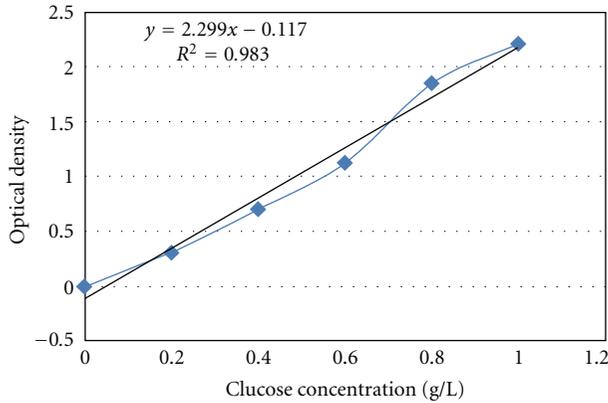


FIGURE 2: Standard curve of glucose concentration versus optical density at 540 nm.

The good marginal integrity of open-sandwich restorations filled with Biodentine is likely due to the outstanding ability of the calcium silicate materials to form hydroxyapatite crystals at the surface [23]. When formed at the interface between the restorative material and the dentin walls, these crystals may contribute to the sealing efficiency of the material. Just after mixing, the calcium silicate particles of Biodentine, like all calcium silicate materials, react with water to form a high-pH solution containing  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ , and silicate ions. In the saturated layer, the calcium silicate hydrate gel precipitates on the cement particles, whereas calcium hydroxide nucleates [24]. The calcium silicate hydrate gel polymerizes over time to form a solid network, while the release of calcium hydroxide increases the alkalinity of the surrounding medium. Saliva, like other body fluids, contains phosphate ions [25]; an interaction between the phosphate ions of the storage solution and the calcium silicate-based cements leads to the formation of apatite deposits that may increase the sealing efficiency of the material [23]. A micro-Raman spectroscopy study revealed crystalline apatite and calcite at the surface of a calcium silicate cement stored in phosphate-buffered saline for 28 days [26]. Therefore, the soaking solution needed to be buffered to prevent alkaline erosion of the cement, needed to be frequently renewed to maintain the ongoing diffusion from the restorative material toward the surrounding medium and needed to contain phosphate ions to permit hydroxyapatite formation [27]. Since the effects of various anions and cations on the dissolution process of calcium silicate-based cement have not yet been explored, it was decided to store the teeth in phosphate-buffered saline instead of artificial saliva [28]. In addition to the formation of apatite crystals, the nanostructure of the calcium silicate hydrate may also explain the good sealing qualities of the calcium silicate cement [29]. The small size of forming gels may contribute to better spreading of the material onto the surface and better fitting to dentin walls; a slight expansion of the calcium silicate-based materials in water and phosphate-buffered saline has also been demonstrated [30].

In order to achieve a valid comparison, the experimental protocol must reproduce optimal clinical conditions. Thus, prior to microleakage assessment, in this study the teeth

TABLE 3: Glucose concentration in the receiving medium after 1 h diffusion through the gingival margin of open-sandwich restorations filled with a calcium silicate-cement or a resin-modified glass ionomer cement. A statistically significant difference was found among the four groups. The groups with the same superscript letter were not statistically different.

Material	Glucose concentration (g/L)
Calcium silicate cement	$0.074 \pm 0.035^b$
Resin-modified glass ionomer cement	$0.080 \pm 0.032^b$
Positive control	$0.450 \pm 0.320^c$
Negative control	$0 \pm 0.002^a$

underwent a mechanical loading associated with simultaneous thermocycling that was performed with a device already in use for the assessment of composite resistance to oral wear [31] and restoration microleakage [22]. Previously, simultaneous load cycling and thermocycling were decisive factors in microleakage evaluation [32]. Axial loading was performed with a 50-N force in the present study because class II restorations were evaluated [33]; this loading corresponds to the process that occurs *in vivo* on natural teeth when clenching in centric occlusion [34]. The teeth were stored at 4°C which was not clinically relevant and may have reduced the chemical reaction rate. Nevertheless, a low storage temperature was indispensable because pilot studies had shown that it was difficult to control bacterial growth for periods as long as one year. This is why 0.5% chloramine.T was added to the storage medium. In addition, this was counterbalanced by a very long storage time. Thermomechanocycling was performed before aging when the dentin/material interface was not yet filled with material resulting from calcium silicate or resin-modified glass ionomer cement dissolution. This likely increased the thermomechanocycling efficiency without favoring any group because both materials have a long setting time [35].

Since the dye penetration studies are questionable, a new assessment method was applied to evaluate marginal integrity. The glucose test was first proposed in dentistry to detect apical leakage of endodontic treatments [36]. With this model, it was possible to quantify the microleakage, an improvement over earlier qualitative scoring methods such as dye penetration. Glucose was chosen as a tracer because of its small molecular size (molecular weight 180 g/mol) and because it serves as a nutrient for bacteria. If glucose were able to diffuse from the oral cavity to the pulpal space, bacteria that survive cavity preparation and filling could multiply and cause recurrent caries and pulpal inflammation. The enzymatic method used in the present work is very sensitive. First, glucose is oxidized to gluconic acid and hydrogen peroxide by glucose oxidase. Second, hydrogen peroxide reacts with o-dianisidine in the presence of peroxidase to form a colored product. Third, oxidized o-dianisidine reacts with sulfuric acid to form a more stable colored product. The intensity of the pink color measured at 540 nm is proportional to the original glucose concentration. The detection limit of the method was  $2 \times 10^{-3}$  g/L which is very low compared to

the data recorded in the present study and warrants the quality of controls. The difference of levels of magnitude of the data recorded with the negative and positive controls showed that the method is valid for the assessment of open-sandwich restoration marginal integrity.

It can be concluded from the present study that resin-modified glass ionomer cement and the calcium silicate cement allowed similar glucose diffusion at the interface between the restorative materials and the dentin walls. The calcium silicate cements may become a material of choice for restorative dentistry in the coming years and compete with the resin-modified glass ionomer cement.

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## Clinical Study

# In Vivo Disintegration of Four Different Luting Agents

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The purpose of this study was to evaluate the disintegration of luting agents. An intraoral sample holder was made having four holes of 1.4 mm diameter and 2 mm depth. The holder was soldered onto the buccal surface of an orthodontic band, which was cemented to the first upper molar in 12 patients, average age 26 years. The holes were filled with a zinc phosphate (Phosphate Kulzer), a glass ionomer (Ketac Cem), a resin-modified-glass ionomer (Fuji Plus), and a resin cement (Calibra). Impressions were made at baseline, and 6, 12, and 18 months from which epoxy replicas were made, which were scanned with an optical scanner. Total volume loss was calculated. The rank order of mean volume loss was as follows: Phosphate cement > Ketac Cem = Fuji Plus = Calibra. Cement type and time had statistically significant effects on volume loss of cements ( $P < 0.001$ ). Under in vivo conditions, zinc phosphate cement disintegrated the most, whereas no significant difference was observed for glass ionomer and resin-based cements. As intraoral conditions are considerably less aggressive than experimental laboratory conditions, the erosion behavior of glass ionomer cement was found to be similar to the resin-based cements in contradiction to previous laboratory results.

## 1. Introduction

Solubility and disintegration of luting cements are important factors that determine the clinical longevity of crowns, bridges, posts, and so forth. Numerous articles have appeared in the literature evaluating these properties [1–11]. Among the factors that complicate direct comparisons when employing in vitro test are differences in the chemical composition of the various cements and hence different mechanisms of breakdown. The most common laboratory test on solubility and disintegration can be found in the ADA specification no. 8 in which a cement disc is immersed in distilled water for 24 h, after which the solute is gravimetrically determined [12]. The ADA test does not give an indication of the fully hardened cement, either in water or in oral fluids [13]. Many investigators have reservations about this test and have used different methods [6, 14–18]. Some authors designed a laboratory test that better correlated with in vivo disintegration results or varied the test circumstances by using longer periods and/or different pH levels [6, 14, 18].

In addition, artificial and natural saliva [15] were used, and passive or agitation conditions were introduced [6, 7, 9, 14, 15]. Other investigators [16–18] concentrated on the erosion factor and directed jets of media onto the surfaces of specimens. The results demonstrated that the combined solubility/erosion in a liquid flow results in different relative deterioration rates compared to a nonflowing medium [18].

Attempts to correlate in vitro solubility with the rate of degradation in the oral cavity has been limited. One of the early reports dates back to 1969 [2], in which cast removable partial dentures were used. The cements were placed in relatively large cavities located on the lingual surface of the denture and worn for 30 days by 8 patients. The appliances were weighed, and the loss of cement was calculated. Cements that were tested were zinc phosphate, silicate, and zinc oxide eugenol cements, and the changes reported were subsequently 5–30 mg·cm<sup>-2</sup>, 0 mg·cm<sup>-2</sup>, and 20–100 mg·cm<sup>-2</sup> [2].

Other studies that focused on in vivo disintegration of luting cements have used various designs such as placing

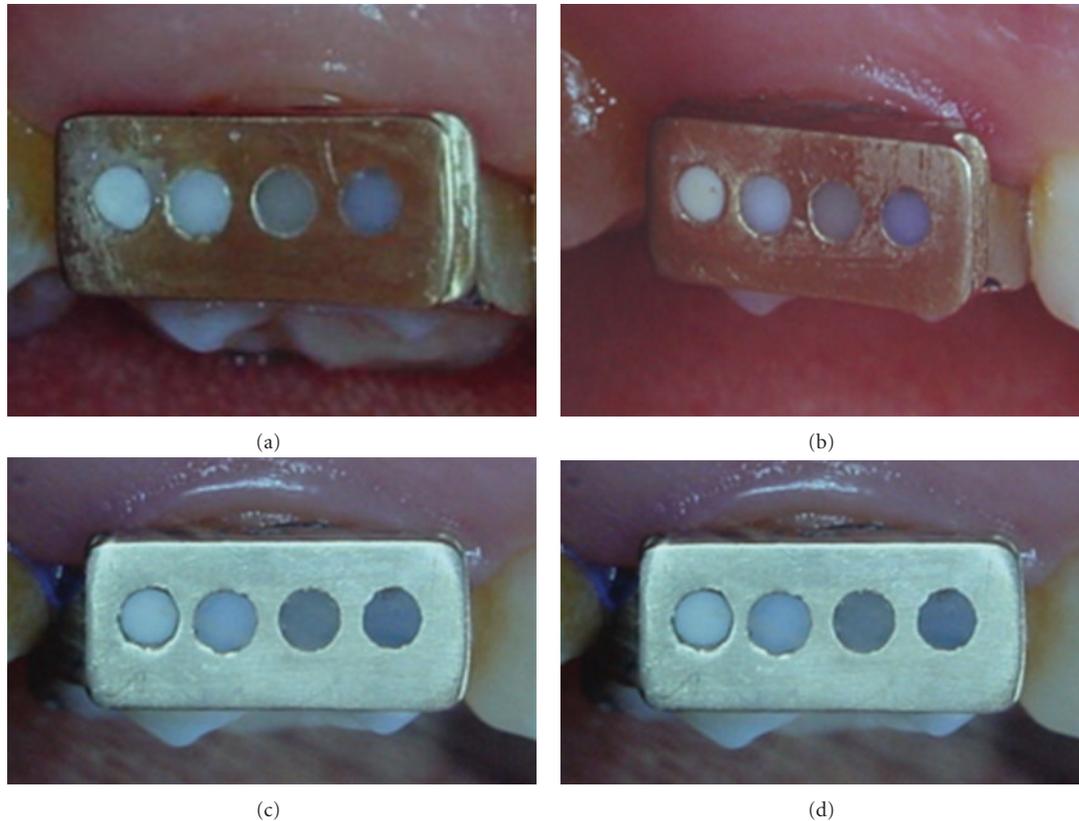


FIGURE 1: Cement holder (a) at baseline; (b) after 6 months; (c) after 12 months; and (d) after 18 months. Cements were placed in uniform cylindrical openings. In sequence from left to right are zinc phosphate, glass ionomer, resin-modified glass ionomer, and resin cement.

cements into molds of different sizes either in removable or fixed partial dentures. Table 1 is a summary of the current literature evaluating *in vivo* disintegration of luting cements. A comparison of the results from relevant literature is challenging due to the difference in tested cements, evaluation times and variation in exposed surface areas. However, most studies have focused on *in vivo* disintegration of acid-base reaction cements demonstrating that from lowest to highest disintegration the sequence was glass ionomer cement < zinc phosphate < polycarboxylate cement [5, 7, 10, 19].

The introduction of new adhesive techniques and materials for use in restorative dentistry also led the development of new dental cements that are resin based. The ability to adhere to multiple substrates, high strength, and insolubility in the oral environment are major advantages of the resin-based luting agents. However, the number of clinical studies regarding the disintegration of these new luting agents is limited. Roulet and Wälti [8] used a “drawer” made from type II gold in the pontic of thirteen sanitary-type fixed partial dentures. They showed the behavior of a composite resin and a glass-ionomer cement in the oral environment in which composite resin exhibited improved resistance to solubility in comparison to glass ionomer material during 28 months of *in vivo* conditions.

The aim of this study was to evaluate the *in vivo* disintegration of resin-based luting cements (resin-modified-glass ionomer and resin cement) in comparison to zinc phosphate and a glass ionomer cement over a period of 18 months.

## 2. Subjects and Methods

Twelve intraoral sample holders (9 mm high, 5 mm wide, and 2.5 mm deep) designed as a receptacle for the test materials were fabricated in gold (Biopontostar alloy, Bego, Bremen, Germany). Each holder had four holes, 1.4 mm in diameter and 2 mm deep, prepared perpendicular to the surface. Each holder was soldered to the buccal surface of an orthodontic band which was suitable for placement on the upper first molar. Each opening contained a different cement: (1) a zinc phosphate cement (Phosphate), (2) a glass ionomer cement (Ketac Cem), (3) a resin modified glass ionomer cement (Fuji Plus), and (4) a resin cement (Calibra) (see Figure 1).

The luting agents were mixed at room temperature on a glass slab by the same person, using a stainless steel spatula with a stiff blade. The powder/liquid (P/L) ratios were in accordance with the manufacturers' recommendations and are presented in Table 2. Powder and liquid were weighed using an electronic digital microbalance (Scaltec, Hamburg, Germany) with a measuring accuracy of 0.1 mg. To reduce the possibility of voids, a spiral lentulo was used for insertion of the cement into the openings. After a slight overfill was established, a mylar strip covered the cement and was pressed down with a glass plate, which was retained with a spring clamp. During setting, the sample holder was placed in an incubator with a relative humidity of 100% at 37°C for 10 minutes. The resin-based cement was inserted into the openings as described above followed by light curing for 40 s

TABLE 1: In vivo disintegration studies on luting cements.

Author, year	Exposed cement surface area	Duration	Cement	Disintegration
Norman et al. [2], 1969	Large cavity extending from lower premolar to molar region	30 days	ZnP S ZOE/EBA	5–30 mg/cm <sup>2</sup> 0 mg/cm <sup>2</sup> 20–100 mg/cm <sup>2</sup>
Richter and Ueno [3], 1975	3 mm diameter	12 months	SP ZnP ZOE/EBA PC	SP<ZP<PC ≈ ZOE/EBA
Osborne et al. [4], 1978	0.82 mm diameter	6 months	SP ZnP ZOE/EBA PC	SP<ZP<PC< ZOE/EB
Mitchem and Gronas [5], 1978	2 mm diameter	6 months	GIC SP ZnP PC	200 μm 350 μm 600 μm 930 μm
Sidler and Strub [20], 1983	0.8 mm diameter	14 months	GIC ZnP	40–100 μm 500 μm
Roulet and Wälti [8], 1984	1.5 mm diameter	28 months	GIC R (Adaptic) R (Adaptic + Soflex disc)	0,041 mm 0,0086 mm 0,01 mm
Phillips et al. [19], 1987	0.8 mm diameter	6–12 months	GIC SP ZnP PC (High ratio of powder to liquid)	GIC<SP<PC< ZP
Pluim et al. [7], 1984	1.3 mm diameter	6 months	GIC ZnP PC	0,5–1 μm/week 20–22 μm/week 18–30 μm/week
Hersek and Canay [10], 1996	5 mm diameter	8 months	PC ZnP GIC	GIC<ZP<PC

ZOE/EBA, zinc oxide eugenol reinforced with ethoxybenzoic acid; S, silicate cement; SP, silicophosphate cement; PC, polycarboxylate cement; ZnP, zinc phosphate cement; GIC, glass ionomer cement; R, composite resin.

TABLE 2: Luting cements used in study.

Product name	Producer	Batch no.	Type	P/L Ratio (g)
Phosphate cement	Heraeus Kulzer, Werheim, Germany	P: 1650437 L: 1750438	Zinc Phosphate	1.2/0.88
Ketac Cem	3M ESPE, Germany	P: 138783 L: 129918	Glass Ionomer	3.8/1
Fuji Plus Capsule	GC Corporation, Tokyo, Japan	0303262	Resin-modified glass ionomer	2/1
Calibra	Dentsply Caulk, USA	Base: 0208141 Catalyst: 030108	Resin	(Base/Catalyst) 1

P, powder; L, liquid.

(Eliza Light 500, Apoza Enterprise Co., Ltd., Taipei Hsien, Taiwan). After curing or setting, the surface of the sample holder containing the cements was finished to a uniform flat surface on wet 600-grit paper (English Abrasives and Chemicals Ltd., Manchester, England).

The study design had been approved by the Ethics Board of Marmara University, Istanbul, Turkey. The objectives of the study were explained to the patients and informed consent was obtained. Criteria for inclusion included (1) ≥18 years of age, (2) upper first molar free of caries, and (3)

good oral hygiene. Patients were also questioned on their dietary intakes in order to exclude individuals who frequently consumed low pH foods or had bulimia.

Prior to cementation of the appliance an impression was made of the surface of the cement holder using a vinyl polysiloxane impression material (Panasil contact plus, Kettenbach Dental, Germany). The replica made thereof established the baseline. The appliance was then cemented to an upper first molar of each patient. Routine oral hygiene instructions were reviewed and a standard soft

TABLE 3: Mean volume loss (mm<sup>3</sup>) observed for the tested cements as a function of time.

	6 months	12 months	18 months
Zinc Phosphate	0,13 ± 0,05	0,24 ± 0,05	0,31 ± 0,09
Ketac Cem	<b>0,03 ± 0,03</b>	<b>0,05 ± 0,03</b>	<b>0,08 ± 0,06</b>
Fuji Plus	<b>0,02 ± 0,02</b>	<b>0,05 ± 0,04</b>	<b>0,08 ± 0,07</b>
Calibra	<b>&lt;0,005</b>	<b>0,01 ± 0,01</b>	<b>0,02 ± 0,02</b>

Means expressed in bold are not statistically significant.

brush (Colgate Total Soft, Colgate-Palmolive Co.) and a microabrasive toothpaste (Colgate Mint Stripe Gel, Colgate-Palmolive Co.) were supplied. The patients were recalled at 6, 12 and 18 months. At each recall visit, an impression of the cement holder was made intraorally using the previously described impression material. The negative impression was poured with an epoxy resin resulting in a replica of the cements in the holder. A Proscan 2000 A (Scantron Inc.) noncontact optical scanner was used for analyzing the epoxy replicas. A S5/03 sensor was used with a resolution of 0.01 micron and differences between the baseline replicas and the 6, 12, and 18 month samples represented total volume loss. A 2-way analysis of variance and Tukey multiple range tests were performed to distinguish statistically significant differences between the groups ( $P < .001$ ).

### 3. Results

The mean and standard deviations of the volume loss of luting agents are shown in Table 3. The lowest cement loss was recorded for Calibra after 6 months ( $<0.005 \text{ mm}^3$ ), whereas Phosphate cement after 18 months recorded the greatest loss ( $0.31 \text{ mm}^3$ ). Of all luting agents, Phosphate cement showed the highest mean loss of substance at all observation times. Increasing the observation time resulted in a marked increase in loss from the surface of Phosphate cement.

ANOVA showed that cement type, time, and their interactions all had a statistically significant effect on volume loss ( $P < .001$ ). Tukey multiple range test revealed that the volume loss of zinc phosphate cement was statistically significantly greater than Ketac Cem, whereas no significant differences were observed between Ketac Cem, Fuji Plus, and Calibra.

### 4. Discussion

The disintegration of a luting agent is an important factor affecting the long-term durability of a restoration. Mechanical wear due to brushing abrasion and chewing forces, leaching due to chemical erosion, and fatigue of the small amount of luting material at the margins as a result of mechanical loading, are the factors that complicate the disintegration mechanism of a luting agent. In this respect, several in vitro studies [6, 7, 9, 14, 15] have appeared in the literature reporting on the solubility and disintegration of luting agents. There have been attempts at simulating the

complexity of the oral environment in these in vitro tests. Despite in vitro studies supplied knowledge on mechanical properties of the materials used, no in vitro method can totally subject materials to in vivo conditions, since they can not simulate the pH and temperature changes of the oral cavity. Thus, the correlation between the results of in vitro studies and clinical studies has to be questioned.

There are few clinical studies [5, 7, 10, 19, 20] of adequate duration to establish correlation with in vitro testing. In addition, most of the existing in vivo disintegration studies [5, 7, 10, 19, 20] have focused on acid-base reaction cements, and only one clinical study [8] investigating a resin-based cement has been reported. Roulet and Wälti [8] designed a special “drawer”, in the pontic of thirteen sanitary-type fixed partial dentures, to show the behavior of a composite resin and a glass-ionomer cement in the oral environment by excluding the effect of mechanical wear caused by opposing teeth, food, or toothbrushing. A glass-ionomer cement and composite resin were inserted in cavities of the drawer and material loss was measured with a three-coordinate measuring machine after 2, 9, 16, and 28 months. They showed that composite resin exhibited decreased solubility in comparison to glass ionomer material after 28 months evaluation time.

In the present study, disintegration of resin-based luting agents (a resin-modified-glass ionomer and a resin cement) were evaluated in comparison to zinc phosphate and glass ionomer cements over a period of 18 months. To more reliably correlate in vivo data with laboratory conditions, a previous study [11] evaluated the erosion of the same cements by means of immersion in 0.1 M aqueous sodium lactate/lactic acid buffer (pH = 2.74 and 4.0) over a period of 28 days. The results of the current study confirmed that zinc phosphate cement showed higher disintegration in comparison to glass ionomer and resin-based cements. In the in vitro study [11], studying identical cements, zinc phosphate cement also exhibited higher solubility than glass ionomer cement and resin cements in pH values of either 2.74 and 4.0. Various in vitro and in vivo studies have shown that zinc phosphate cement has higher solubility compared to glass ionomer cement [5, 7, 10, 19, 20]. The deterioration of phosphate cement is due to the loss of zinc from the matrix of phosphate cement, whereas the composition of glass ionomer cement remained nearly constant due to the setting reaction between the fluoroaluminosilicate glass and polyacrylic acid [18, 21].

The glass ionomer cement (Ketac Cem) tested in this study did not exhibit significantly higher disintegration

compared to the resin-based luting cements which is in contrast to the findings of in vitro studies [11, 22]. Most in vitro solubility experiments were performed at one or two pH values, mainly at pH 2.7 or pH 4 or higher. Increased solubility at low pH compared to neutral conditions was a common finding for water-based cements, which occurred linear with time [18, 22]. It appears that in vitro experimental designs are static solubility tests, as they use a constant low pH lactate acid. As laboratory conditions are more aggressive than clinical conditions, the aggressive acidic conditions generated greater loss of glass ionomer cement in comparison to resin-based luting cements.

In a recent study, Meşe et al. [21] used a modified ISO 4049 test to evaluate sorption and solubility of 8 resin-based luting agents in two different solutions: 50% ethanol and water. They demonstrated that in water and in an ethanol/water solution, resin-modified glass ionomer cements exhibited higher sorption and solubility as compared to resin-based luting cements. Resin-modified glass ionomer cement, GC Fuji Plus, also exhibited significantly higher solubility when compared to resin-based luting agents in both water and ethanol/water. The authors contributed the significantly higher solubility of Fuji Plus to the likelihood of unpolymerized free monomers being leached out in an aqueous environment. In the present study, no significant differences were observed between glass ionomer (Ketac Cem), resin-modified glass ionomer (Fuji Plus), and resin cement (Calibra). It is postulated that the less aggressive conditions of the oral environment resulted in less erosion of the glass ionomer, resin-modified glass ionomer and resin cements. Intermittent exposure to acidic solutions, salivary flow, and buffering capacity is one of the factors that contributed to less disintegration of the test cements under in vivo conditions. Salivary pH and buffering capacity are believed to be the sole factors that can effect cement solubility. However, Pluim [18] showed in an in vivo study that there was no correlation between salivary pH and buffering capacity and cement solubility. They concluded that cement erosion was due to bacterial and dietary acids and not to dissolution by saliva. Thus, the differences between the cement loss values of individuals can be attributed to the differences between their dietary intakes.

It would be an error to predict in vivo disintegration of luting materials from this in vivo experiment, as the exposed cement surface of 1.4 mm in diameter was a factor many times larger than a clinically acceptable margin of 40  $\mu$ m. Thus, the level of erosion should be considered within the context of exposed surface area. The luting agents used in fixed prosthesis with clinically acceptable marginal adaptation will be subjected to less tooth brush abrasion and wear from chewing and will most probably show lower disintegration rates.

## 5. Conclusions

The results of this in vivo study support the conclusions that:

- (1) zinc-phosphate cement showed greater disintegration than glass ionomer and resin-based cements

whereas the mean disintegration values of glass-ionomer and resin-based cements were not significantly different,

- (2) as intraoral conditions are considerably less aggressive than experimental laboratory conditions the erosion behaviour of glass ionomer cement was found to be similar with the resin-based cements in contradiction to previous laboratory results.

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