CURRENT STATUS OF DENTAL LUTING CEMENTS

Col David Charlton

Ideal Properties of a Dental Cement

1. low viscosity and film thickness
2. long working time with rapid set at oral temperatures
3. low solubility
4. high compressive and tensile strengths
5. high proportional limit
6. adhesion to tooth structure and restorative materials
7. anticariogenic properties
8. biocompatibility
9. translucency
10. radiopacity

Classification of Cements

zinc phosphate
zinc oxide-eugenol
glass ionomer
zinc polycarboxylate
resin

General Cement-Forming Reaction

Cements are usually formed by an acid/base reaction in which an acidic liquid and a basic powder are combined to produce a matrix of reaction products in which are embedded unreacted powder particles. In most cases, the powders are either zinc oxide or aluminosilicate glasses while the liquids are phosphoric acid, polyacrylic acid, or eugenol.

Many of the common cements used in dentistry just represent different combinations of these powders and liquids as shown in the table below:

		LIQUIDS		
POWDERS		phosphoric acid	polyacrylic acid	eugenol
	zinc oxide	Zinc Phosphate Cement	Zinc Polycarboxylate Cement	Zinc Oxide-Eugenol Cement
	aluminosilicate glass	--------------	Glass-ionomer Cement	--------------

Zinc Phosphate Cement

One of the oldest and most widely used cements, zinc phosphate cement is the standard against which new cements are measured. Commercially available products include Fleck's Zinc (Mizzy), Hy-Bond (Shofu), and Modern Tenacin (LD Caulk).

The set cement consists of a zinc phosphate matrix in which unreacted 2- to 8-micron-diameter zinc oxide powder particles are embedded. Crystals of hopeite, or tertiary zinc phosphate, are found on the surface of the cement.

Composition

Powder

ZnO	90.2%	
MgO	8.2%	Condenses the ZnO during the sintering process
SiO_2	1.4%	Acts as an inactive filler
Bi_2O_3	0.1%	Imparts smoothness to the newly mixed cement
Misc (BaO, Ba_2SO_4, CaO)	0.1%	

Liquid

H_3PO_4	38.2%	
H_2O	36.0%	
H_3PO_4 (with water)	16.2%	
Zn	7.1%	Both aluminum and zinc act as buffers or partial neutralizing agents to reduce the reactivity of the powder and liquid
Al	2.5%	

Advantages

long record of clinical acceptability, high compressive strength, acceptably thin film thickness

Disadvantages

low initial pH which may lead to postcementation sensitivity, lack of an ability to bond chemically to tooth structure and lack of an anticariogenic effect

The pH of newly mixed zinc phosphate cement is under 2, but rises to 5.9 within 24 hours and is nearly neutral at 48 hours.

Repeated opening of the bottle containing the cement liquid or early dispensing of the liquid prior to mixing should be avoided because changes in water/acid ratio can occur due to evaporation of the water; these changes can cause a decrease in pH and an increase in viscosity of the mixed cement.[1]

The lower the temperature of the cement during mixing, the longer will be the working time. This is advantageous because it allows incorporation of more powder into the liquid which results in greater compressive strength and lower solubility of the final cement.

Strength of the cement is almost linearly related to its powder-to-liquid ratio; zinc phosphate cement achieves 75% of its ultimate strength within 1 hour.

Orthodontists often mix the cement using the "frozen slab" technique which greatly extends the working time (by as much as 300%) and allows incorporation of from 65% to 95% more powder into the liquid than normally occurs. This offsets the possible deleterious effects of incorporating water into the mix. Film thickness increases (3 to 5 microns), pH increases, and setting time is shortened.

Water contamination of the cement should be avoided while it is setting. If moisture contaminated, phosphoric acid leaches out of the cement and solubility greatly increases.

Two types of zinc phosphate cement exist:

- Type I: used for cementation of precision castings; ADA Specification No. 8 calls for a film thickness of less than 25 microns
- Type II: used as a base and for luting orthodontic bands; the specification calls for a film thickness between 25 and 40 microns

Working time is approximately 4 to 5 minutes.

The specification also calls for a setting time of from 5 to 9 minutes.

A 1970 study[2] of nearly 800 crown and bridge units cemented with zinc phosphate cement found the following reasons for failure:

- -caries: 36.8%
- -loss of retention (i.e., they had become loose): 12.1%
- -defective margins: 11.3%
- -periodontal disease: 6.8%
- -periapical involvement: 2.9%

The average lifespan of the restorations was 10.3 years.

Zinc Polycarboxylate Cement

Zinc polycarboxylate cement, also known as zinc polyacrylate cement, was one of the first chemically adhesive dental materials. The adhesive bond is primarily to enamel although a weaker bond to dentin also forms. This is due to the fact that bonding appears to be the result of a chelation reaction between the carboxyl groups of the cement and calcium in the tooth structure; hence, the more highly mineralized the tooth structure, the stronger the bond.

When zinc oxide and polyacrylic acid are mixed, hydrated protons formed from ionization of the acid attack the zinc and magnesium powder particles. This causes the release of zinc and magnesium cations which form polycarboxylates that crosslink the polymer chains. The result is a zinc polycarboxylate crosslinked polymer matrix in which unreacted zinc oxide particles are embedded.

Commercially available products include Durelon (3M ESPE), Fleck's PCA (Mizzy), Liv Carbo (GC America), Hy-Bond Polycarboxylate (Shofu), and Tylok-Plus (LD Caulk).

Composition

Powder

is similar to that of zinc phosphate cement powder, consisting of approximately 90% zinc oxide and 10% magnesium oxide

Liquid

is an aqueous solution of from 32% to 43% polyacrylic acid of relatively high molecular weight

Advantages

kind to the pulp, chemically bonds to tooth structure

Disadvantages

short working time, requires separate tooth conditioning step prior to cementation

Working time is approximately 2½ minutes, which is half that of zinc phosphate cement.

The liquid of this cement tends to be viscous because it is a partially polymerized polyacrylic acid.

Although many of these cements are quite viscous after mixing, they achieve an acceptable film thickness because they are pseudoplastic and exhibit a decrease in viscosity when sheared.

The powder contains up to 4% stannous fluoride which acts primarily as a strengthening agent; the fluoride does not impart an anticariogenic effect because the cement leaches fluoride in an amount equivalent to only 10% to 15% of the fluoride leached by a glass-ionomer cement.

Zinc Oxide-Eugenol Cement

Zinc oxide reacts with water to produce zinc hydroxide which then combines with eugenol to produce zinc eugenolate. Within this matrix are found unreacted zinc oxide powder particles. The fact that zinc eugenolate readily hydrolyzes to form free eugenol and zinc hydroxide accounts for the fact that this is one of the most soluble cements. A standard zinc oxide-eugenol temporary filling material has the following composition:

Composition

Powder

ZnO	69.0%
white rosin	29.3%
zinc stearate	1.0%
zinc acetate	0.7%

Liquid
eugenol 85.0%
olive oil 15.0%

Two compositional changes can be made to the powder and liquid to increase the strength of the mixed material to allow it to be used as a permanent luting agent. Either ortho-ethoxybenzoic acid can be added to the liquid and alumina to the powder or poly(methyl methacrylate) powder can be added to the powder. These altered zinc oxide-eugenol materials have the following compositions:

Alumina and ortho-ethoxybenzoic acid reinforced
powder: 70% zinc oxide
30% alumina

liquid: 62.5% ortho-ethoxybenzoic acid
37.5% eugenol

Polymer reinforced
powder: 80% zinc oxide
20% poly(methyl methacrylate)

liquid: 85% eugenol
15% olive oil

Advantages
obtundent effect on the pulp, good short-term sealing
Disadvantages
weak, soluble

Examples of commercially available zinc oxide-eugenol cements include Opotow Alumina EBA (Teledyne Getz), Super EBA (Bosworth), and Fynal (LD Caulk).

Caulk's Fynal is a polymer-reinforced zinc oxide-eugenol cement.

Water is necessary for the cement-forming reaction to occur and both water and warm ambient conditions accelerate the setting reaction.

Zinc acetate is also an accelerator of the setting reaction.

Many researchers question the wisdom of using this cement as a permanent luting agent because of its high degree of solubility.

Resin Cement

As a general rule, resin cements are the best choice for luting ceramic restorations.[3] This conclusion is based on three types of research: laboratory studies measuring the fracture resistance of restorations luted with resin versus other types of cements; clinical studies; and laboratory studies evaluating the sealing/strengthening effect of resin cements. The resin cements were first developed in the early 1950s for use as crown and bridge luting agents but had poor physical properties (high polymerization shrinkage and excessive leakage) because of their low percentage filler content. Modern products are more highly filled and have better physical properties. Resin cements are either visible light-activated, chemically- activated, or dual-activated (both visible light- and chemically- activated). Visible light-activated cements are generally reserved for the luting of cast ceramic, porcelain, and resin composite veneers or for other light-transmitting restorations that are thin enough (i.e., 1.5-mm thick) to transmit light. The chemically-activated forms are used for the cementation of: resin-bonded fixed partial dentures; thick (i.e., 2.5-mm-thick) cast ceramic, porcelain, and resin composite restorations; and metal restorations. Dual-activated resin cements are used for luting thin to moderately-thick (i.e., from 1.5-mm- to 2.5-mm-thick) cast ceramic, porcelain, and resin composite restorations where light penetration may be limited.

Commercially available products include: Biomer (Dentsply/Caulk), Comspan (Dentsply/Caulk), Variolink II (Ivoclar Vivadent), Enforce (Dentsply/Caulk), Calibra (Dentsply/Caulk), Ultra-Bond (Den-Mat), Mirage FLC (Chameleon), Insure (Cosmedent), RelyX Veneer Cement (3M ESPE), C&B-Metabond (Parkell), Nexus 2 (SDS/Kerr), RelyX ARC (3M ESPE), RelyX Unicem (3M ESPE), Panavia 21 (Morita), and Illusion (Bisco).

Composition

BIS-GMA or urethane dimethacrylate resins filled from 30% to 80% with generally submicron filler particles.

Advantages

high compressive strength, low solubility

Disadvantages

irritating effects on the pulp, high film thickness

Dual affinity resins, the so called "Japanese acrylics", are resin cements whose manufacturers claim they have the ability to chemically bond to both tooth structure and metals. These cements contain adhesive monomers such as MDP, HEMA, and 4-META and include such products as Panavia 21 (J. Morita) which contains MDP and C&B-Metabond (Parkell) which contains 4-META. These cements may be of clinical benefit in providing increased retention for restorations when minimal retention form exists because several studies have found these cements to be more retentive than zinc phosphate, glass-ionomer, and conventional resin cements.[4-6]

Panavia, first marketed in 1983, has been described as a phosphonated methacrylate or a modified phosphate ester of BIS-

GMA. The first form of the product was marketed from 1983 to 1994 and consisted of a powder and a liquid. The powder was a BIS-GMA based resin filled to 76% by weight with quartz particles. Also present in the powder was a benzoyl peroxide initiator. The liquid consisted of aliphatic and aromatic methacrylates, phosphate monomers, tertiary amine and sulfinate activators, and stabilizers. Also in the liquid was the bifunctional adhesive monomer 10-methacryloyloxydecyl dihydrogen phosphate (also known as MDP or M10P). Adhesion to tooth structure appeared to result from both mechanical and secondary bonding (hydrogen bonding and/or Van der Waals forces). Panavia's bond strength depended on the substrate. Bond strength to metal varied from 20 to 40 MPa while bond strength to tooth structure ranged from 8 MPa (dentin) to 28 MPa (enamel).
The new product, Panavia 21, differs from its predecessor because it has an enamel/dentin primer and is provided as two pastes rather than as a powder and a liquid. The pastes are supplied in a unique, automated, syringe-type dispenser that facilitates consistent paste-to-paste dispensing. A cartridge refill for the dispenser provides enough cement for approximately 55 applications. The primer comes in two separate bottles and is mixed just before use. It contains hydroxyethyl methacrylate (HEMA), N-methacryloyl 5-aminosalicylic acid (5-NMSA) and MDP. Morita claims that the primer enhances bond strength to dentin which had been relatively low with the old product. When using Panavia 21 to bond resin-bonded fixed partial dentures to tooth structure, the metal should not be etched. Etching results in a lower bond strength, possibly because mechanical irregularities in the metal trap air and water which inhibit Panavia 21's polymerization. If the casting is a base metal, simply air abrade it with 50-micron aluminum oxide at from 60 to 100 psi and then ultrasonically clean it. If the casting is a noble metal, it should be air abraded, tin plated, and ultrasonically cleaned. Tin plating enhances mechanical as well as chemical bonding because it increases roughness of the surface. Pen-shaped tin plating devices are available and include the Kura-Ace Mini from Morita for $600.00 and the Micro-Tin from Danville Engineering for $139.95. When bonding to uncut enamel, etching of the tooth structure is recommended. A 40% phosphoric acid etchant in a syringe is provided with the product. If the enamel has been prepared, only primer is applied; no etching is necessary. Dentin is treated by applying the primer for 60 seconds and then drying it. Panavia 21's polymerization is strongly inhibited by oxygen, so a polyethylene glycol gel, Oxyguard II, must be used to cover the exposed cement to ensure completeness of polymerization. The gel contains a sulfinate activator that is said to hasten setting of the covered cement. Panavia 21 is available in three shades: TC (tooth color) which is very translucent; EX (standard white) which is partially translucent; and OP (opaque) which is opaque. All three shades are said to be radiopaque. Film thickness is reported by the manufacturer to be

19 microns however an average value of 46 microns has been measured in the DIS laboratory. Shelf life is approximately 18 months when the product is refrigerated.

C&B-Metabond is based on the 4-META/MMA-TBB system developed in Japan in which bonding occurs as monomers flow into demineralized intertubular and peritubular dentin. The product contains a dentin activator solution (citric acid/ferric chloride), enamel etchant (phosphoric acid), base (4-META, MMA), catalyst (tributyl borane), and tooth colored and clear powders (PMMA). When using this cement for the luting of resin-bonded fixed partial dentures, prepare the casting surface as described for Panavia; the tooth surface should be treated with the enamel etchant or dentin activator as appropriate. Film thickness may intentionally be varied from 15 to 50 microns by altering powder-to-liquid ratio.

Dual-cure resin cements achieve only a portion of their polymerization from chemical curing.[7] It is, therefore, very important to ensure that they are adequately light activated.

Generally, film thickness has been reduced for the resin cements due to the use of smaller filler particles and incorporation of diluent monomers,[8] however some products still cause excessive film thicknesses, especially if used improperly.

It is recommended that patients be advised against loading restorations newly luted with chemically-activated resin cements because early bond strengths are weak and need a period of 24 hours to fully mature. Generally, the patient should be told to be careful to avoid loading for the first hour. It is also suggested that excess marginal cement be removed before it sets to avoid damaging the weak early bond.[9]

Cementing provisional restorations with eugenol-containing temporary cements remains controversial. Although it is clear that free eugenol inhibits resin polymerization, several studies have found no effect on resulting resin-to-dentin bond strengths.[10,11]

Glass-ionomer Cement

The development of these cements was announced in a 1972 article in the British Dental Journal written by Wilson and Kent. They are hybrids of the silicate cements and the polycarboxylate cements. By developing the glass-ionomer cements in this way, it was hoped that they would possess the advantages of both the silicate cements (translucency and fluoride release) and the polycarboxylate cements (kindness to the pulp and chemical adhesion to tooth structure). Available products include: Ketac-Cem (3M ESPE), Fuji Type I (GC America), and Glasionomer Type I (Shofu).

The setting reaction of these cements occurs in three overlapping phases. Initially, hydrated protons formed from the ionization of polyacrylic acid attack the glass particles converting their peripheries into silica-based hydrogels and causing the release of aluminum, calcium, and fluoride ions. In the second phase, these ions migrate out of the hydrogel and into the aqueous cement phase where they precipitate out as the pH increases. The resulting calcium and aluminum polycarboxylates ionically crosslink the polymer chains to form the basic cement matrix. The calcium polycarboxylates form first for several reasons: the calcium ions are released in greater quantities from the glass than are the aluminum ions; the calcium ions have a bivalent rather than trivalent charge (as do the aluminum ions) which enables them to migrate faster into the aqueous cement phase; and the calcium ions do not form as stable fluoride complexes as do the aluminum ions. As a result, they are more readily available to perform the crosslinking. The aluminum polycarboxylates are stronger and more stable than the calcium polycarboxylates and, therefore, the cement's properties improve over time as the aluminum polycarboxylates form in greater numbers. In the third step of the reaction, a slow hydration of both the polycarboxylates and the hydrogel occurs which also results in a slow, but steady improvement in the cement's physical properties.

Composition

Powder

consists of an ion-leachable calcium aluminofluorosilicate glass with a maximum grain size of between 13 and 19 microns; the powders silicon dioxide, aluminum oxide, and calcium fluoride are combined to produce the primary cement powder; fluoride content ranges from 10% to 23%.

Liquid

is an aqueous solution of polymers and copolymers of acrylic acid.

Advantages

chemical bond to enamel and dentin, anticariogenic effect, coefficient of thermal expansion similar to that of tooth structure, high compressive strength, low solubility

Disadvantages

low initial pH which may lead to postcementation sensitivity, sensitivity to both moisture contamination and desiccation

Some forms of the glass-ionomer cements are called "water mixed" or "water hardened"; their polyacids have been dehydrated and added to their powders. This is done by the manufacturer to lengthen shelf life by preventing gelation and to reduce viscosity of the mixed cement. The liquid of these cements is tartaric acid or distilled water. One example is Ketac-Cem marketed by 3M ESPE.

Film thickness is generally less than 25 microns.

Never chill the liquid of a non-water mixed glass-ionomer cement because it will exhibit an increase in viscosity.

The latest development involving the use of glass ionomers as luting agents has been the introduction of self-cured hybrid resin/glass-ionomer products such as Fuji Plus (formerly Fuji Duet, GC America), FujiCem (GC America), and RelyX (formerly Vitremer Luting Cement, 3M ESPE). Hybrid resin/glass ionomers were initially introduced as light-activated liners/bases and later as dual-activated restorative materials. These new cements have several advantages compared to traditional glass-ionomer luting agents such as Ketac-Cem, Ketac-Cem Aplicaps, and Fuji Cap I. They have greater tensile strength and are less brittle. In addition, they release at least as much fluoride as traditional glass ionomers,[12] are less soluble, and are less sensitive to moisture contamination and desiccation.[13] Although the three brands are similar in that they are all self setting (i.e., self curing), differences exist between them in many ways (e.g., how the prepared tooth is treated prior to luting and the number of clinical uses for the cement). For example, no additional treatment is performed prior to using RelyX. With Fuji Plus, however, the prepared tooth surface must be treated immediately before luting with an acidic conditioner. While RelyX is used only for luting, Fuji Plus is used for luting as well as a liner/base. FujiCem is the only one of the three that is a two-paste system; the other two are powder and liquid. It is important to know that these cements should not be used to lute all-ceramic crowns such as IPS Empress (Ivoclar) or In-Ceram (Vident) because of clinical fractures. Most researchers believe this is due to post-placement hydrolytic expansion of the cement caused by water sorption.

Additional Cement Facts

Cement Rankings

Compressive Strength (highest to lowest):
resin; glass ionomer; zinc phosphate; polycarboxylate; ZOE

Solubility (lowest to highest):
resin; glass ionomer; zinc phosphate; polycarboxylate; ZOE

Cement film thickness is dependent upon powder-to-liquid ratio, powder particle size, and pressure generated during seating of the casting.

The most important clinical property of a cement is solubility.

Generally a cement dissolves when the solvent attacks the cement's matrix, however with zinc polycarboxylate cements, both the matrix and powder particles are attacked.

Increasing a cement's powder-to-liquid ratio generally has the following effects:

- compressive strength: increases
- solubility: decreases
- pH: increases
- viscosity: increases
- film thickness: increases
- setting time: shortens it because more powder surface area is available for acid interaction

When using zinc phosphate, resin, and glass-ionomer cements, researchers have found that increasing the roughness of the internal surfaces of castings using coarse-grit aluminum oxide in an air abrader significantly increases the retention of the castings compared to using fine-grit aluminum oxide.[14]

The roughness of the preparation also affects retention. In another study using zinc phosphate cement, retention was significantly greater for castings cemented to preparations made with a diamond bur than to those prepared with a carbide bur.[15]

One way to reduce the potential for post-cementation sensitivity with zinc phosphate and glass-ionomer cements is to use a resin-based desensitizer on the prepared tooth prior to luting. Recent research has found that this type of desensitizer does not adversely affect crown retention.[16]

Cement Summary and Indications for Use

Zinc Phosphate Cement: a good choice for routine prosthodontic use; has a long, positive clinical history but must be used properly to avoid postcementation sensitivity.

Zinc Polycarboxylate Cement: acceptable for single units or short span fixed partial dentures; chemically bonds to tooth structure and is extremely kind to the pulp; recommended for cases involving hypersensitive teeth.

Zinc Oxide-Eugenol Cement: acceptable for single units and short span fixed partial dentures; has an obtundent effect on the pulp but low strength and moderately high solubility.

Resin Cement: excellent choice for luting porcelain, cast ceramic, and composite resin restorations; possesses high strength and low solubility but can cause pulpal sensitivity.

Glass-Ionomer Cement: excellent for general prosthodontic use especially when the patient would benefit from fluoride release; exhibits low solubility with the ability to chemically bond to tooth structure and leach fluoride; avoid using when teeth are hypersensitive.

Recommended Cements for Clinical Use

Encapsulated Glass-Ionomer Cement: for routine use. Examples are Fuji Cap I, Ketac-Cem Aplicap, and Ketac-Cem Maxicap.

Zinc Polycarboxylate Cement: for cases involving hypersensitive teeth or where preparations encroach on the pulp. Examples are Durelon and Tylok Plus.

Adhesive Resin Cement: for cases where inadequate retention/resistance form exists after preparation (i.e., preparation is overtapered and/or short). Examples are Panavia 21 and C&B-Metabond.

References

1. Hondrum SO. Effects of evaporation on the properties of water-based dental luting agents. Gen Dent 2000;48:286-290.
2. Schwartz NL, Whitsett LC, Berry TG, Stewart JL. Unserviceable crowns and fixed partial dentures: life-span and causes for loss of serviceability. J Am Dent Assoc 1970;81:1395-1401.
3. Burke FJT, Fleming GJP, Nathanson D, Marquis PM. Are adhesive technologies needed to support ceramics? An assessment of the current evidence. J Adhes Dent 2002;4:7-22.
4. Tjan AH, Li T. Seating and retention of complete crowns with a new adhesive resin cement. J Prosthet Dent 1992;67:478-483.
5. Caughman WF, O Connor RP, Williams HA, Rueggeberg FA. Retentive strengths of three cements using full crown preparations restored with amalgam. Am J Dent 1992;5:61-63.
6. Eakle WS, Giblin JM. Retention strength of tin plated gold inlays bonded with two resin cements. Gen Dent 2000;48:406-410.
7. El-Mowafy OM, Rubo MH, El-Badrawy WA. Hardening of new resin cements cured through a ceramic inlay. Oper Dent 1999;24:38-44.
8. McComb D. Adhesive luting cements - classes, criteria, and usage. Compend Contin Ed Dent 1996;17:759-773.
9. Burrow MF, Nikaido T, Satoh M, Tagami J. Early bonding of resin cements to dentin - effect of bonding environment. Oper Dent 1996;21:196-202.
10. Mayhew JT, Windchy A, Sleet HW, Gettleman L. Effect of sealant cement and irrigation agents on dentatus post retention luted with Panavia 21 [Abstract]. J Dent Res 1996;75:55.
11. Ganss C, Jung M. Effect of eugenol-containing temporary cements on bond strength of composite to dentin [Abstract]. J Dent Res 1996;75:127.
11&12.
12. Robertello FJ, Coffey JP, Lynde TA, King P. Fluoride release of glass ionomer-based luting cements in vitro. J

Prosthet Dent 1999;82:172-176.
13. McComb D. Adhesive luting cements - classes, criteria, and usage. Compend Contin Ed Dent 1996;17:759-773.
14. Juntavee N, Millstein PL. Effect of surface roughness and cement space on crown retention. J Prosthet Dent 1992;68:482-486.
15. Felton DA, Kanoy BE, White JT. The effect of surface roughness of crown preparations on retention of cemented castings. J Prosthet Dent 1987;58:292-296.
16. Swift EJ, Lloyd AH, Felton DA. The effect of resin desensitizing agents on crown retention. J Am Dent Assoc 1997;128:195-200.