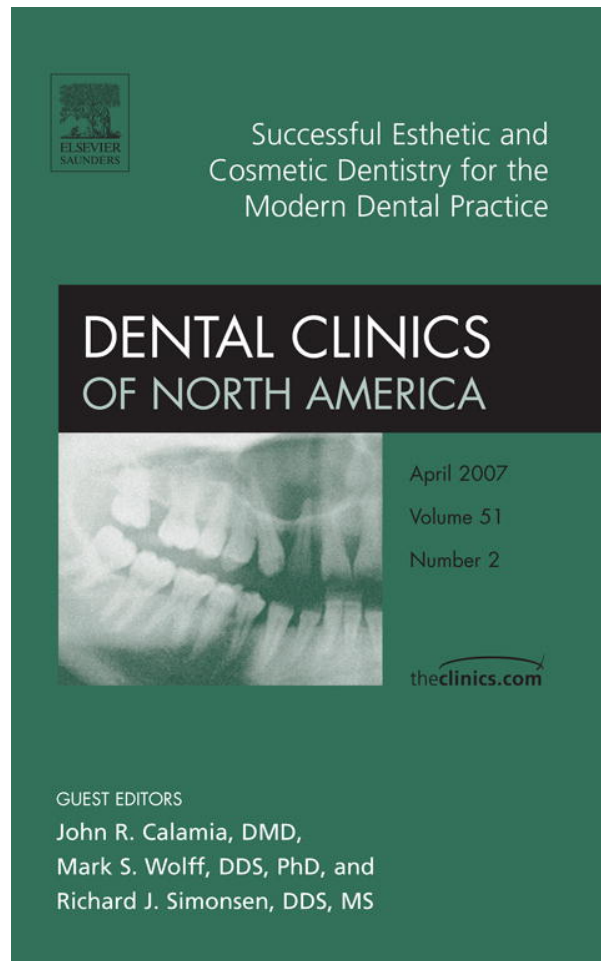


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Cements for Use in Esthetic Dentistry

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Dental cements are designed to retain restorations, appliances, and posts and cores in a stable and, presumably, long-lasting position in the oral environment. Retention mechanisms for restorations secured by cements are reported to be chemical, mechanical (friction), and micromechanical (hybridized tissue). Retention of the restoration is usually achieved by a combination of two or three mechanisms depending on the nature of the cement and the substrate.

Acceptable clinical performance of dental cements requires that they have adequate resistance to dissolution in the oral environment, strong bond through mechanical interlocking and adhesion, high strength under tension, good manipulation properties such as acceptable working and setting times, and biologic acceptability for the substrate [1].

Many dental cements are commercially available, including resin-based and non-resin-based cements. Traditionally, zinc phosphate cement has been regarded as the most popular luting material despite its well-documented disadvantages, particularly, solubility and lack of adhesion [2]. Glass ionomer luting cements are also of great interest for clinicians, principally because these materials release fluoride that may prevent recurrent caries [1–3]. Resin-based cements are generally used for esthetic restorations (ceramic or resin based) and have become popular because they have addressed the disadvantages of solubility and lack of adhesion noted in previous

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materials [1]. The advent of adhesive luting cements has considerably expanded the scope of fixed prosthodontics.

Restorative dentistry is constantly undergoing change, driven in part by new clinical applications of existing dental materials and the introduction of new materials. Currently, no commercially available luting cement is ideal for all situations. There has been considerable discussion on the properties and performance of these cements. Table 1 summarizes a variety of dental cements with their respective characteristics.

This article discusses the advantages and disadvantages of most common dental cements. Emphasis is given to resin-based cements for esthetic restorations owing to the large amount of discussion of these agents in the recent literature.

Zinc phosphate cements

Zinc phosphate cement has the widest range of applications in luting restorations, which includes the cementation of fixed cast alloys and porcelain restorations. It may also be used as a cavity liner or base to protect pulp from mechanical, thermal, and electrical stimuli [4]. The retention of restorations cemented by zinc phosphate materials (nonadhesive luting material) is largely dependent on the geometric form of the tooth preparation that limits the paths of displacement of the cast restoration.

Zinc phosphate cement can be regarded as the first “self-etch cement,” because its acidity is capable of demineralizing the dentin surface and exposing collagen fibrils [5]; however, a traditional hybrid layer cannot be produced, because the acidic liquid segregates from the particles that are not capable of infiltrating the interfibrillar spaces. In fact, owing to the filtration phenomenon observed with these materials and concerns regarding possible hazard to the pulp, it has been recommended that dentin be covered with a layer of copal varnish before luting with zinc phosphate cement [4,6]. The adhesive potential of zinc phosphate cement was not appreciated in former usage in prosthodontics.

Because of its long-time use and excellent clinical performance, zinc phosphate cement has been regarded as the gold standard for comparative studies. If evidence-based dentistry is strictly followed, zinc phosphate cement has far more evidence of success than any other luting material available. Apart from this strong rationale for its use, disadvantages of the cement include the negative biologic effects (pulp irritation), the lack of antibacterial action, the lack of adhesion, and the elevated solubility in oral fluids [2]. Nevertheless, zinc phosphate cements continue to deliver successful results when used to retain metal crowns, porcelain-fused-to-metal crowns, bridges, cast posts, and other restorations. Even some all-ceramic restorations can be luted with zinc phosphate cements (eg, In-Ceram, Procera), but relevant long-term clinical data on their performance are still lacking.

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Table 1
Current material classes of dental luting cements

Materials	Area of application	Strengths	Weaknesses
Zinc phosphate cement	Routine application in metal-supported crowns, bridges, and posts	Over 100 years of clinical experience	Occasional postoperative sensitivity Low hardness High solubility
Glass ionomer cement	Routine application in metal-supported crowns and bridges Limited application with high-strength ceramics during curing	20 Years of clinical experience Fluoride release Molecular bonding to the tooth substance Minimal dimensional change Simplicity of use Medium strength Good routine cement	Occasional postoperative sensitivity Sensitivity to water and mechanical loading
Resin-modified glass ionomer cement	Routine application in metal-supported crowns, bridges, and posts (esthetic) Limited application with lab-manufactured composite works Limited application with high-strength ceramics	Good routine cement Fluoride release Medium strength Molecular bonding to the tooth structure Low solubility Less technique sensitive Little postoperative sensitivity	Moisture-sensitive powder Swelling Not indicated for most ceramics
Adhesive resin cement	All metal-based ceramics, lab-manufactured composite works and posts (esthetics)	Over 10 years of successful application High adhesion qualities with pretreatment High hardness Low solubility High mechanical properties Good esthetics	Difficulty of handling Requires use of separate primers or adhesives Too strong for certain applications No fluoride release Occasional postoperative sensitivity

Author's Personal

Glass ionomer cements

Glass ionomer cements are commonly used for cementation of cast alloy and porcelain restorations. These cements exhibit several clinical advantages [7], including physicochemical bonding to tooth structures [7,8], long-term fluoride release, and low coefficients of thermal expansion [7,9]; however, their low mechanical strength compromises their use in high stress-bearing areas [7,10].

The major benefit of glass ionomer cements is their ability to adsorb permanently to the hydrophilic surfaces of oral hard tissues, offering the possibility of sealing margins developed at the tooth-material interfaces during restorative and luting procedures [11]. Improvements in the formulation of the original glass ionomer cements have led to the development of hybrid materials that contain varied amounts of resin monomers. If the material can set properly by the acid-base reaction without the need of light activation, the material can be regarded as a resin-modified glass ionomer cement. Otherwise, if the setting mechanism is mainly directed by the light curing of the resin monomers, the material is more likely a polyacid-modified resin composite (compomer) and does not fit into the class of glass ionomer cements.

Resin-modified glass ionomer cements are indeed improved materials when compared with traditional glass ionomer cements. They represent the most used material among its class. The advantages of resin-modified glass ionomer cements include a dual-curing mode (light activated and self-curing), fluoride release from the cement, and higher flexural strengths in comparison with conventional glass ionomer cements. They are also easier to handle, including the fact that they are capable of bonding to composite materials. Although widely used as dental cements, glass ionomer cements have some disadvantages. One problem is that they do not always promote sufficient bond strength to enamel and dentin [12]. The other disadvantage is their ability to absorb water from the surrounding environment. Premature exposure to water leads to leaching of ions and swelling and weakening of the cement, whereas loss of water leads to shrinkage and cracking of the cement [13]. In general, bond strengths are greater to enamel than to dentin, leading to the conclusion that bonding occurs to the mineral phase of the tooth via chelation of calcium ions at the surface of the hydroxyapatite [14].

Glass ionomers remain the only materials that are self-adhesive to the tooth tissue without any surface pretreatment. Nevertheless, pretreatment with a weak polyalkenoic acid conditioner has been demonstrated to significantly improve their bonding and sealing efficiency [15–17]. The additional conditioning step becomes more important when coarse cutting diamonds are used and consequently thicker smear layers are produced. The increase in bonding efficiency must be attributed in part to a “cleaning effect” in which loose cutting debris is removed and to a partial “demineralization”

effect in which the surface area is increased and microporosities for micromechanical interlocking or hybridization are exposed. More recently, chemical adhesion to partially demineralized dentin has been demonstrated [15–17] that favors the stability of the bond. In this respect, glass ionomers can be considered as adhering to tooth tissue through a self-etch approach [15–18]. The basic difference with the resin-based self-etch approach is that glass ionomers are self-etching through the use of a relatively high molecular weight polycarboxyl-based polymer, whereas resin-based self-etch adhesives make use of acidic low molecular weight monomers [18].

Glass ionomer cements exhibit properties beyond bonding to tooth structure. They can potentially be used as matrices for the slow release of active species, as has been previously documented for fluoride ions. They are able to bond chemically to surface active glasses, which have in their compositions substances such as calcium, sodium, phosphorus, and silicon. The combination of glass ionomer cements with these bioactive glasses (BioGlass or BAG) results in glass ionomer cements with surface activity properties [19]. The bioactive nature of BioGlass and glass ceramics is related to their ability to form a bonelike apatite layer on their surfaces in the body environment [20]. Some findings suggest that BioGlass could be used for remineralizing damaged dentin, and that it has potential as a filler component in mineralizing restorative materials such as glass ionomer cements [21].

A recent study [19] demonstrated that resin-modified glass ionomer cements containing BioGlass have the potential to mineralize dentin. In contact with saliva, these materials promote calcium phosphate precipitation on the dentin surface. The ability of these materials to precipitate minerals on the dentin surface may make them promising resources for the treatment of dentinal hypersensitivity and for lining deep cavities in dentin.

Chlorhexidine is another example of a substance that can be incorporated into glass ionomer cements. Chlorhexidine can subsequently be released, resulting in the antibacterial properties of the cement. Additionally, chlorhexidine-releasing materials may be somewhat beneficial in preventing the action of host-derived matrix metalloproteinases in the degradation of exposed collagen [22,23]; however, the addition of chlorhexidine to glass ionomer cement may alter its properties. A recent study showed that the incorporation of chlorhexidine in glass ionomer cement resulted in increases in the working and setting times and a decrease in compressive strength [24]. Additional studies are evaluating the benefits of incorporating active substances and fillers in the basic formula of glass ionomer cements. Clinicians may expect several improvements in glass ionomer cement-based materials in the near future. For a more complete update, readers are advised to review the September 2006 issue (volume 34, issue 8) of the *Journal of Dentistry*, which carries the proceedings of the Second European Glass-Ionomer Conference held in May of 2004.

Table 2
Varieties of adhesive resin cements

Product	Company (location)	Bonding system per manufacturer	Indications	Curing mode	Additional features
Bistite II DC	Tokuyama (Tokyo, Japan)	Primer 1A+1B + Primer 2	A, I, and M	Dual-curing system	Different shades Metal primer
BisCem	Bisco (Schaumburg, Illinois)	Self-adhesive	A, B, I, M, and P	Dual-curing system	Fluoride releasing Auto-mixing syringe
Calibra	Dentsply/Caulk (Milford, Maine)	Prime & Bond NT	A, B, I, M, P, and V	Dual-curing system	Different shades Fluoride releasing
C&B Cement	Bisco (Schaumburg, Illinois)	All-Bond 2 One-Step	A, B, I, M, and P	Self-curing system	Dual-syringe mixer Fluoride release
Cement-Post	Angelus (Londrina, PR, Brazil)	Angelus Primer + Angelus Adhesive	A, B, M, and P	Self-curing system	Angelus silane
Choice	Bisco (Schaumburg, Illinois)	All-Bond One-Step	A, B, M, and V	Dual-curing system	Different shades Try-in paste
Duo-Link	Bisco (Schaumburg, Illinois)	All-Bond 2 One-Step/Plus	A, I, and P	Dual-curing system	Dual-syringe mixer
Illusion	Bisco (Schaumburg, Illinois)	One-Step	A, B, I, M, P, and V	Dual-curing system	Color modifier paste Try-in paste Viscosity modifier
Multilink	Ivoclar Vivadent (Schaan, Liechtenstein)	Primer A + B	A, B, I, M, and P	Self-curing system	Multilink Automix
Nexus 2	Kerr (Orange, California)	OptiBond Solo Plus	A, B, I, M, P, and V	Dual-curing system	Different shades Fluoride releasing Try-in paste Dual syringe

Panavia F 2.0	Kuraray (Okayama, Japan)	ED Primer	A, B, I, and M	Dual-curing system	Fluoride releasing Different shades Light shade especially for veneers
RelyX ARC	3M ESPE (St. Paul, Minnesota)	Adper Single Bond	A, B, I, M, and P	Dual-curing system	Clicker Dispenser RelyX Veneer-exclusive veneer indication
RelyX UNICEM	3M ESPE (St. Paul, Minnesota)	Self-adhesive	A, B, I, M, and P	Dual-curing system	Activator/applier combination pack Capsule mixing unit (for use with capsules) Different shades
Super-Bond C&B	Sun Medical (Moriyama, Japan)	Monomer + catalyst V + polymer powder	A, B, I, M, P, and V	Self-curing system	Super-Bond C&B Quick Monomer V-PRIMER concurrently for precious metal alloys Porcelain Liner M concurrently for porcelain
Variolink II	Ivoclar Vivadent (Schaan, Liechtenstein)	Excite adhesive system	A and I	Dual-curing system	Different shades Two degrees of viscosity Try-in paste Variolink II Veneer-exclusive veneer indication

Abbreviations: A, all-ceramic crown-inlay/onlay; B, bridge; I, indirect resin composite; M, metal; P, post and core; V, veneer.

Resin cements

Resin cements have become popular clinically owing to their ability to bond to both the tooth structure and restoration. The use of indirect restorations retained with adhesive procedures constitutes a substantial part of contemporary dental treatments. Metal and metal-free crowns, inlays, onlays, veneers, posts, and even resin-bonded fixed prostheses are now routinely bonded to tooth substrates by the use of adhesive resin cements (Table 2) [25]. The successful use of resin cements depends on several aspects related to the bonding mechanisms to both dental and restorative substrates. Recent publications have addressed many previously unknown issues that are key factors in determining the reliability of luting procedures with resin cements. These issues are discussed in the following sections.

Bonding to tooth structure: incompatibility issue

Except for glass ionomer cements and two self-etch resin cements available for clinicians (Unicem, 3M ESPE [St. Paul, Minnesota], and BisCem, Bisco [Schaumburg, Illinois]), all other resin cements require an adhesive agent to bond esthetic restorations to dental structures. The majority of adhesive systems used with resin cements are simplified systems because of clinical trends for reduced steps during adhesive procedures. These simplified adhesives are basically of two types: (1) etch and rinse single-bottle systems and (2) “all-in-one” self-etch adhesives. They are both somewhat acidic and hydrophilic in nature. During cementation, the acidic groups in the uncured layer of simplified adhesive agents (due to the presence of oxygen) compete with peroxides for aromatic tertiary amines of the luting agent, resulting in an acid-base reaction between the adhesive and the resin cement (Fig. 1A). This reaction minimizes appropriate co-polymerization

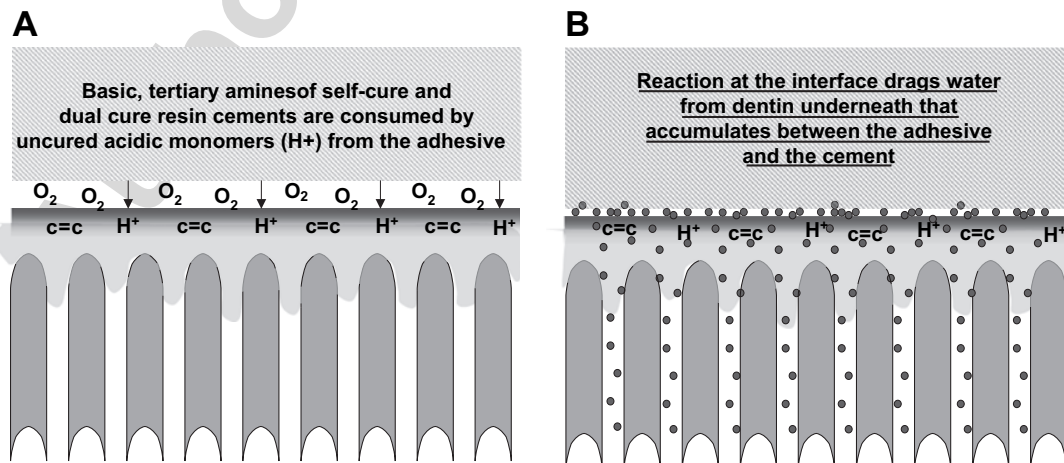


Fig. 1. (A) Basic tertiary amines of self-cure and dual-cure resin cements are consumed by uncured acidic monomers (H^+) from the adhesive. (B) Reaction at the interface drags water from dentin underneath that accumulates between the adhesive and the cement.

between the two [26–28]. Additionally, the hydrophilic characteristic of such adhesive systems functions as a permeable membrane. This hydrophilic behavior permits the flux of water through the adhesive after polymerization [29,30]. The presence of water at the interface between the adhesive and the cement compromises the total bonded area and proper polymerization of the cement (Fig. 1B). Water droplets may accumulate at the interface and may function as stress raisers, leading to failure of the adhesive-cement interface [30]. This permeability problem could be partially solved by the application of an intermediate layer of a relatively more hydrophobic, nonacidic, low viscosity resin separating the acidic layer of adhesive from the composite resin cement [30,31]; however, this extra layer of adhesive may create a thick film, which would be a concern during the cementation procedure of esthetic restorations.

The water that accumulates at the interface derives from the hydrated dentin underneath (Fig. 1B). The negative effect of such water permeation on the bond strength of resin cements to dentin has been confirmed in in vitro studies [29,30]. These studies demonstrated improved bond strengths when the teeth were purposely dehydrated in ascending ethanol series before bonding. Because such dehydration of dentin is impossible to achieve in daily practice, clinicians are advised to use less permeable adhesive systems such as the three-step etch and rinse or two-step self-etch when bonding self- or dual-cured resin cements to dentin [30,31]. The major advantage of these systems is that they include a layer of a relatively more hydrophobic and nonacidic resin as the third or second step. This additional layer will not cause an adverse reaction with the basic amines of the cement and will reduce the permeability of the adhesive layer to water transudation from the dentin.

The incompatibility issue has brought up concerns for several clinical procedures. Practitioners should comprehend that unsuccessful treatment occurs owing to a combination of factors. First, permeability problems will not be in effect when esthetic restorations are cemented on metal, ceramic, or fiber-reinforced resin posts or cores. Moreover, problems when luting veneers with simplified adhesive systems should not be frequently experienced because clinicians typically use light-cured resin cements, and they are ideally bonded to enamel. The worst clinical scenario would occur when luting posts using simplified adhesives associated with dual-cured resin cements. Proper bonding to the apical portion might be severely compromised by the adverse interactions between adhesive and luting composite due to a lack of light exposure. Without light activation, dual-cure resin cements will actually function as exclusively self-cure cements. In this mode, the cement will take longer to cure, allowing more time for the adverse reaction and transudation of water from dentin to occur. Not surprisingly, some clinicians experience dislodgement of the recently luted post when they attempt to remove the provisional crown from a reconstructed preparation made with posts luted with resin cements (Fig. 2A–G). Based on

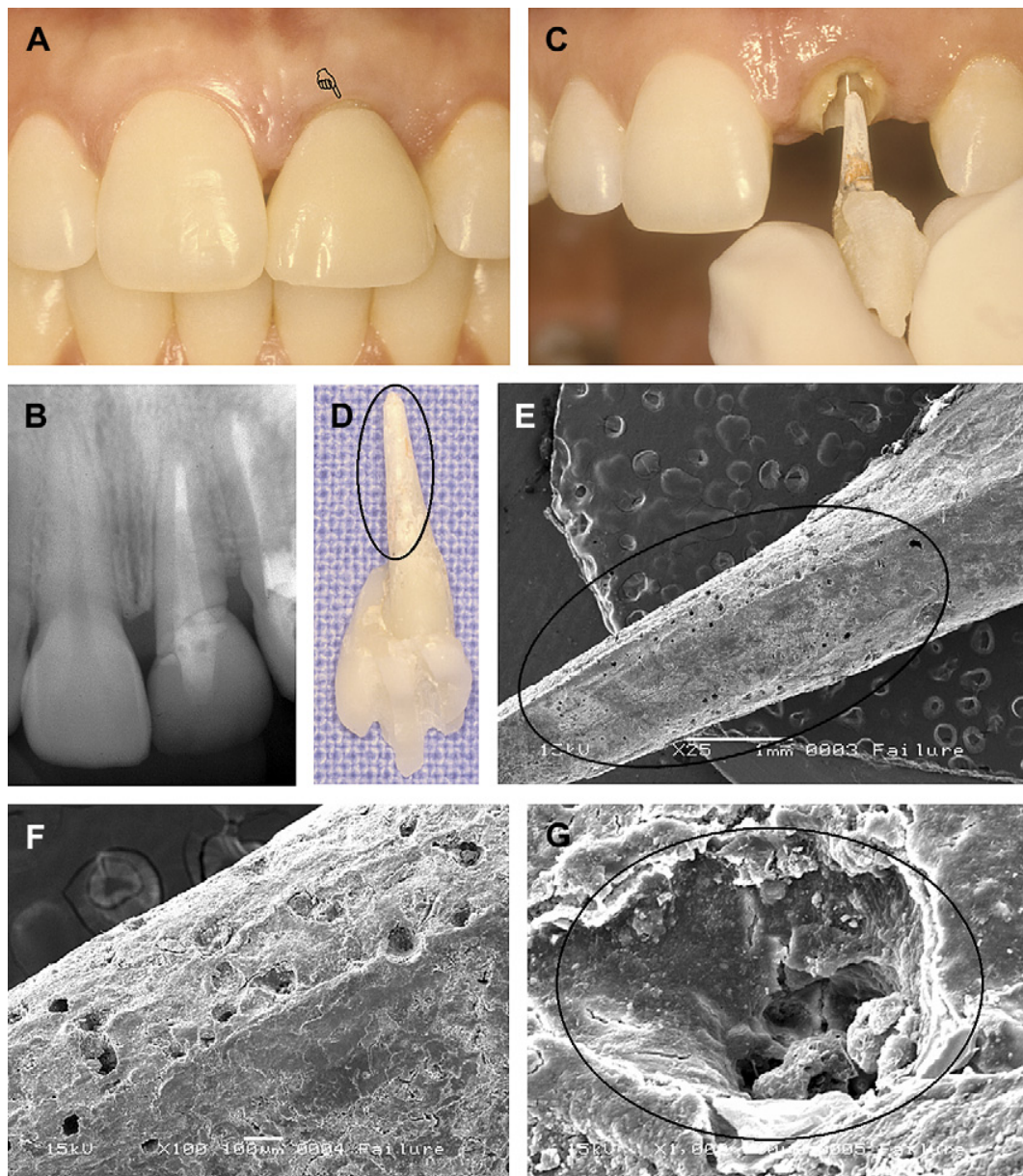


Fig. 2. Clinical case of dislodgement of luted post. (A) Clinical view of dislodgement of resin cement (Panavia) luted post (*black pointer*). (B) Radiographic view of the clinical case. (C, D) Closer view of the post dislodged. Note (*black circle*) the presence of resin cement on the post. (E) Scanning electron microscope image of the dislodged post. Note (*black circle*) the massive presence of bubbles, especially on the middle and apical thirds. (F) Closer view of (E), the presence of bubbles, which could be attributed to the water that migrated through the adhesive layer and to the poor polymerization that occurred, especially in the middle and apical thirds, denoting the so-called “emulsion polymerization.” (G) Higher magnification of (F). The water droplets are kept trapped in the poorly polymerized cement (*black circle*), leading to degradation and crack spots along the adhesive-cement interface. (Courtesy of Dr. Estevam A. Bonfante, Brazil.)

those limitations, some studies have suggested the development of a specific bonding system for this purpose [32,33]. Recent studies have shown that the push-out resistance of posts luted with resin cements was similar, regardless of the use of an adhesive system to bond to root dentin [32,33]. They have

concluded that the retention of a post to a root canal is mainly determined by friction rather than by adhesive mechanisms. A truly adhesive luting procedure can only be achieved when clinicians combine the use of resin cements with three-step etch and rinse or two-step self-etch bonding systems.

Bonding to the surface of esthetic restorations (ceramics)

The ability of the combination of resin cement/adhesive system to adhere to dental ceramics depends on the microstructure of the esthetic restoration and the surface treatment applied [34]. Although roughening the surface by grinding or the application of airborne particles is considered a way for improved adhesion for most esthetic materials, silanization appears to be only effective for silica-based ceramics [35]. A durable and reliable bond for dental ceramics is usually attempted via two principal mechanisms—micromechanical attachment to porosities originated from hydrofluoric acid etching [36] with or without grit blasting—both associated with a silane coupling agent. Research evaluation of the bond strength between ceramic restorations and resin composite cements has resulted in varied conclusions as to the effect of varied surface treatments [36]. Controversy in the literature [36–39] focuses on the possible inefficacy of the silane coupling agent and operator's handling of the procedure.

Silane coupling agents are bi-functional molecules capable of bonding to the OH groups on ceramic surfaces and copolymerizing with the organic portion of the resin cement or adhesive. Silane primers contain a silane agent (usually γ -methacryloxypropyl-trimethoxy silane), a weak acid, and high amounts of solvents. To be effective, the silane agent must be hydrolyzed by the weak acid. Once hydrolyzed, silane primers have a limited shelf-life, and effectiveness progressively decays over time. The effectiveness of pre-hydrolyzed, single-bottle silane primers is unpredictable if the user is not aware of when the solution was activated. Clinically, the only indicator seems to be the appearance of the liquid. A clear solution is useful, whereas a milky-like solution should be discarded [35]. An alcoholic solution (one-bottle systems) stays transparent, and the signs of alterations cannot be identified; therefore, two-bottle solutions are preferred. Practitioners should strictly respect the expiration date and follow the manufacturer's recommendations for silane systems.

Understanding how the silanization process occurs on ceramic surfaces is of great importance to improve the effectiveness of silanes. When silane is applied to a ceramic surface and dried, three different structures are formed at what is called the interphase layer [40]. The outermost layer consists of small oligomers that can be washed away by organic solvents or water at room temperature [37]. Closer to the glass surface there is another layer of oligomers that is hydrolyzable. To avoid hydrolysis of this layer after cementation, which could compromise the coupling of the

cement with the ceramic, some authorities recommend that it be removed with hot water before bonding to silanized ceramic [37,41]. Attached to the glass is a third layer, a monolayer, which is covalently bonded to the silica phase of the ceramic and is hydrolytically stable [37]. This remaining monolayer of silane is not removed by the previously mentioned procedures and is responsible for the actual bond between the ceramic and the adhesive/cement system.

Because it is not possible to clinically control the application of a monolayer of silane, undesirable excess must be removed before bonding. This removal can be achieved by several methods. One way is to apply the silane followed by hot air drying ($50 \pm 5^\circ\text{C}$) for 15 seconds for proper solvent evaporation. One then rinses with hot water (80°C) for 15 seconds followed by another hot air drying for 15 seconds [41]. This procedure eliminates water and solvent and washes away any unreacted silane (excess) primer components [41]. Alternatively, silane excess can be removed during the try-in step.

The try-in procedure is known to be a contaminant step; therefore, it has been recommended that it be performed before silanization. Clinicians generally perform the try-in step after receiving the surface-etched (hydrofluoric acid) ceramic restoration from a dental laboratory. Nevertheless, the hydrofluoric acid-treated ceramic surface is hydrophilic and more prone to be contaminated if the hydrophilic try-in paste is applied before the silanization step; therefore, ceramic surfaces should be silanized before the try-in procedure. Once properly silanized, the ceramic surface becomes hydrophobic, and the try-in paste can be removed easily by ultrasonic cleansing. Current scientific evidence [42] shows that if the try-in step is performed after silanization, bond strengths increase significantly. A possible explanation is the fact that the try-in procedure removes the excessive layers of silane from the ceramic surface [42]. Removal of this excess permits proper coupling of the resin cement with the monolayer silanized ceramic surface, improving the bond strength. Moreover, silane treatment alone seems to be effective to improve bond strengths to ceramic. When the try-in step is involved, it should be done after silanization, followed by ultrasonic cleansing for better bond strength.

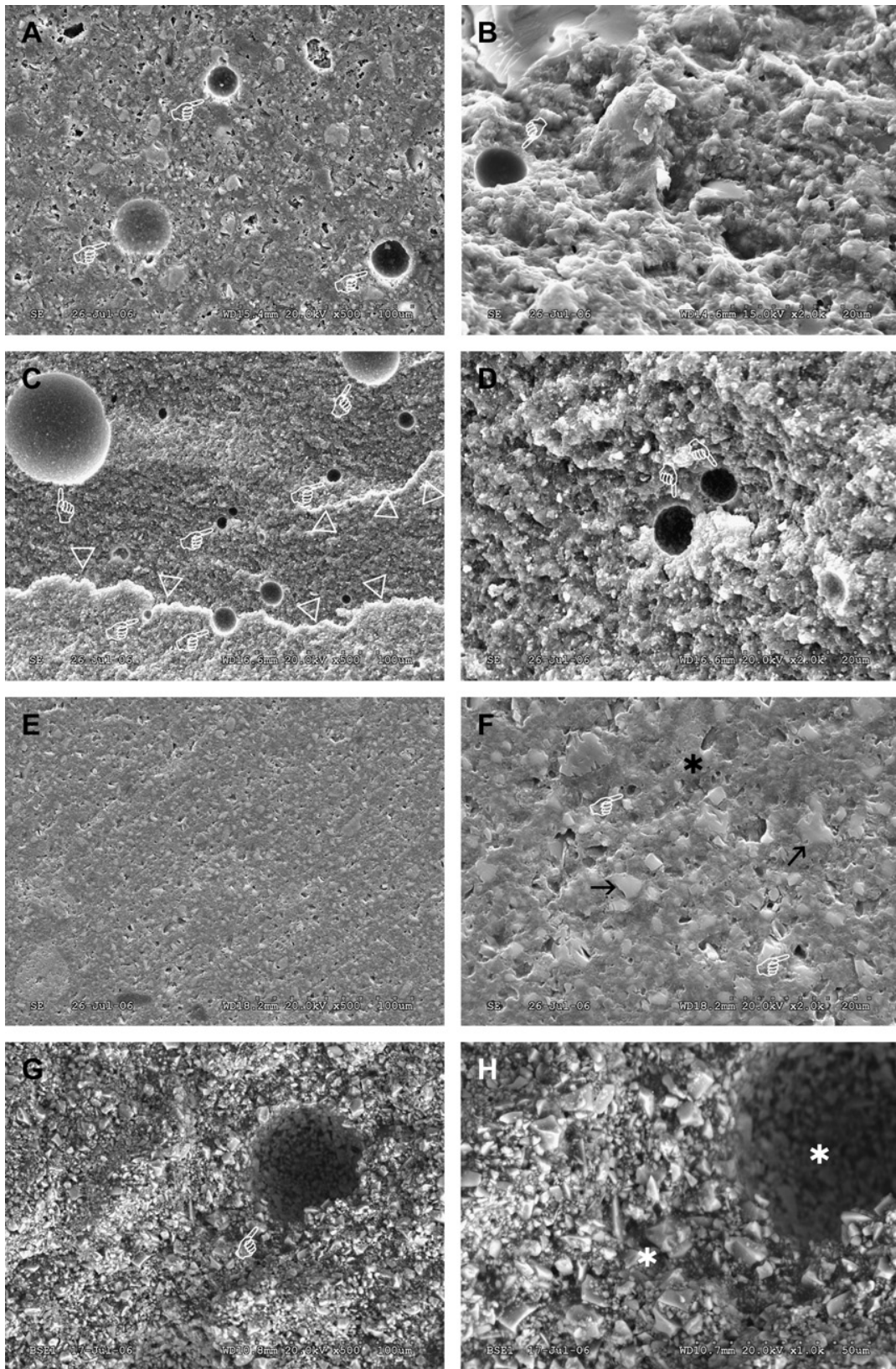
Curing protocol for resin cements

Adhesive resin cements are available in light-cure, auto-cure, or dual-cure formulations, and their selection is based primarily on the intended use [43]. When comparing these cements, light-cure products offer the clinical advantages of extended working time, setting on demand, and improved color stability. Nevertheless, the use of light-cure cements is limited to situations such as cementing veneers or shallow inlays in which the thickness and color of the restoration do not affect the ability of the curing light to polymerize the cement [44,45].

Dual-cure resin cements are indicated when delivering restorations where material opacity may inhibit sufficient light energy from being transmitted to the cement [46]. In these situations, light intensity reaching the cement may be sufficient to begin the polymerization process, but an autopolymerizable catalyst is needed to ensure a maximal cure. Limited information has been published on the light-curing potential of dual-cure cements. Although early research suggested that the auto-cure system alone was not sufficient to achieve maximum cement hardening [47,48], recent literature indicates that the curing kinetics of dual-cure resin cements are more complex than previously thought. Some studies indicate that the light activating some dual-cure cements appears to interfere with the self-cure mechanism and restricts the cement from achieving its maximum mechanical properties [42].

Some dual-cure cements show their self-cure mechanism to be somehow limited when light activated in the dual-cure mode. This limitation may compromise the final mechanical properties of the resin cements [49,50]. One study [50] evaluated the degree of conversion (DC) of various resin cements at different cure circumstances. The Duolink (Bisco, Schaumburg, Illinois), RelyX ARC (3M ESPE, St. Paul, Minnesota), and Illusion (Bisco, Schaumburg, Illinois) resin cements cured well regardless of the activation mode (light cured, dual cured, or self-cured). These cements achieved maximum DC even in areas where the light could not reach. The Variolink (Ivoclar Vivadent, Schaan, Liechtenstein) and Choice (Bisco, Schaumburg, Illinois) cements showed similar DC when light cured or dual cured, but the DC was lower when those cements were allowed to self-cure alone, indicating that these cements would have their polymerization compromised and should be avoided in situations where the light cannot reach. Additionally, Calibra (Dentsply/Caulk, Milford, Maine) showed a poor DC when light activated in the dual-cure or sole light-cure mode. The maximum DC was obtained when the cement was allowed to self-cure alone. This information is of great importance for clinical practice because light activation of this cement is recommended by the manufacturer. Whether the same phenomenon occurs with other resin cements remains to be demonstrated. Although such information is not available for all resin cements on the market, it is advisable to delay light curing of dual-cure cements to the maximum time clinically possible. In this way, premature light activation will not interfere with the self-cure mechanism, and the cements requiring light activation for maximum DC will receive that energy after the waiting period.

Interestingly, alterations in the DC during different curing modes do not necessarily change the mechanical properties of the cements [50]. It seems that there is no linear relationship between the DC and the level of crosslink in the polymer network [51]. Nevertheless, cements that do not cure properly with light activation or that have a compromised self-cure mechanism may experience an adverse chemical reaction and permeability when associated with simplified adhesive systems. Clinically, this implies that the longer the resin cement takes to set, the greater the chance



of adverse effects when coupling resin cements to simplified adhesives. Once again, these concerns could be reduced or even eliminated if clinicians used three-step etch and rinse or two-step self-etch adhesives.

Concerns regarding mixing and working time

Resin cements are often designed for specific applications rather than general uses. They are formulated to provide the handling characteristics required for particular applications. Figs. 3A–H show a series of scanning electron micrographs of different resin cements after mixing and subsequent polymerization. Entrapped voids due to mixing can be seen on polished or fractured regions of the set cement. Although entrapment of voids can be beneficial to reduce the shrinkage stresses generated at the thin cement layer [52], they can also function as stress raisers during tension or compression, generating crack propagation and, consequently, degradation of the cement interface. Voids are also observed in cements that use automatic mixing. Reduction of air bubble inclusion may be obtained with the use of resin cements that present an auto-mixing tip and deliver the mixed paste through a syringe-type tip directly on the surface.

The setting mechanism of dual-cure resin cements is usually based on a redox reaction of benzoyl peroxide with aromatic tertiary amines (represented by catalyst and base paste, respectively). One or both pastes contain a light-sensitive compound (camphorquinone) responsible for initiating the light-cure setting mechanism. After the pastes are mixed together and until light is activated, the adequate working time is controlled by inhibitors of the self-cure reaction or by the amount of peroxide and aromatic tertiary amines. Both the inhibitors and peroxides are organic chemical compounds susceptible to degradation upon storage; therefore, resin cements have a limited storage, and the setting mechanism of the cements may fluctuate during this time. In vitro evidence indicates that both the working time and setting time may be significantly altered upon storage, particularly if the storage temperature is far above that recommended ($>18\text{--}22^{\circ}\text{C}$). Some cements present a shortened working time/setting time, whereas others present an extended working time/setting time [50]. This observation might be due to the instability of their components during storage time. Degradation of

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 Fig. 3. Scanning electron microscope images showing surface topographies of four different resin cements after mixing and curing. White pointers show entrapped bubbles due to mixing. (A) Polished surface (500× magnification) and (B) fracture area (2000× magnification) of Panavia F 2.0. (C) Fractured area of Variolink resin cement. Two fracture lines (*opened arrows*) occurring on the matrix and contouring entrapped bubbles. (D) Higher magnification (2000×) of entrapped bubbles. (E, F) Polished surface of RelyX ARC (500× and 2000× magnification). Filler particles (*black arrows*) adhered to resin matrix (*black asterisks*) are evident. (G, H) Magnification images (500× and 1000×) of RelyX Unicem. Huge amount of particles (*white asterisks*) without resin matrix in between can be seen even inside the enormous entrapped bubble.

peroxide would extend the working time/setting time, whereas degradation of inhibitors would shorten them. The implications of such changes on the mechanical properties of the resin cements are unknown; however, clinicians handling resin cements with a shortened working time may experience some clinical difficulties. On the other hand, increased adverse chemical reactions and permeability problems may be expected for resin cements with an extended working time and setting time.

Resin cement and water sorption phenomenon

When an all-ceramic crown is cemented into a patient's mouth, the assembly ceramic/cement/adhesive/tooth will be subjected to a watery environment. Resin composite cements should have not only low solubility and high color stability but also low water sorption because of esthetic and functional reasons [53]. The water sorption phenomenon has been demonstrated to have an important effect on the properties of composite resin cement after a long period of time [54,55]. This phenomenon diminishes significantly the flexural strength of resin composites. The reduction of flexural strength as well as modulus of elasticity [56] may be critical for thick areas of resin cement. Scientific evidence shows that absorbed water works as a plasticizer for the cements, creating unsupported areas underneath restorations and consequently increasing the chance of fracture of restorations under mastication forces. Clinicians should keep the cement film as thin as possible even in the inner aspect of esthetic restorations to minimize the consequences of the plasticizing phenomenon for resin cements [57]. The water sorption phenomenon of resin cements may also result in hygroscopic expansion [56,58] of the cement, but the influence of that hygroscopic expansion on the long-term durability of dental cements and, consequently, the esthetic restoration is not yet known.

Clinicians should be aware that cements that present an extended working time or setting time do not cure properly with light activation or have a compromised self-cure mechanism and will be affected by hygroscopic issues. Incomplete polymerization and nonconversion of monomer may result in loss of resin, and this may affect the biologic compatibility of the resin material [59]. Scientific evidence [60] has demonstrated that reducing the time for polymerization of light-cure cements to 75% of that recommended by the manufacturer may facilitate fluid uptake and dissolution of the resin, leading to staining and breakdown of the material resulting in failure of esthetic restorations. For that reason, maximum polymerization of the resin cement is crucial to minimize the water sorption phenomenon.

When using dual-cure cements, clinicians should delay the light-curing procedure to the maximum time clinically possible. In this way, the maximum degree of conversion of resin cement may be achieved after light activation, reducing the risk of excessive water uptake.

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