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Strengths of modified amalgam-to-dentin interphases

E. HERDA, Y.K.E. ARIANTO
Materials Science Program, School of Graduate Studies, University of Indonesia, Jl. Salemba 4, Jakarta 10430, Indonesia

R.E. BAIER, A.E. MEYER
Industry/University Cooperative Research Center For Biosurfaces, University at Buffalo, 110 Parker Hall, Buffalo, NY 14214, USA

Amalgam remains the primary dental restorative for nearly 200 000 000 Indonesians. Ground occlusal dentin surfaces of 140 formaldehyde-treated human molars were used to study shear strengths of different adhesive bonds (40: Syntac/Variolink, 40: Amalgambond Plus (AP), 40: AP + microfibre, and 20: Amalcoden) to a spherical high-copper amalgam (Valiant^{tm}, Ivoclar NA). After 24 h at 37 °C/100 RH, restorations were stored for 7 d under one of four different conditions (all 37 °C) : A, 100% RH; B, deionized water; C, 0.9% NaCl solution; D, saliva electrolyte solution. Amalcoden-treated samples were exposed to conditions A and B only. ANOVA and Tukey *post hoc* analysis ($P < 0.05$) were applied. For any single storage condition, AP + microfibre bond strengths were significantly greater than those for other agents tested. Storage condition was a significant variable only for the AP + microfibre; weaker bond strengths were observed for saline-stored samples. Improvement of restorative-to-dentin interfaces, eliminating pulp sensitivity, can result from aldehyde pre-treatment of teeth, as well as from the use of microfibre-filled Amalgambond Plus. These results illustrate the importance of "stabilization" of the entire interphase.

1. Introduction

Amalgam restorations have been used in restorative dentistry for over a century. Although other materials are now available, amalgam is the material most often used for direct restoration of posterior teeth in Indonesia, especially at Public Health and Educational clinics. The reasons for the use of amalgam are many. It is a dimensionally stable material with excellent physical and mechanical properties. Moreover, amalgam is a relatively technique-insensitive material and simple to use. However, amalgam does not adhere to tooth structure. It requires undercut cavity preparations to create mechanical retention.

Recently, several new materials, claimed to be capable of bonding amalgam to tooth structure, have been introduced. Several studies have been performed to evaluate the strength of the bonds these agents make to amalgam and the large variations in results are obtained.

Oilo [1] noted that measured bond-strength values depend on the type and details of the test method, type and quality of dentin, and storage conditions prior to testing, in addition to the quality of the bonding material and how it is handled.

The stress field at the interface between a filling and the cavity wall is always complex, but it can be identified as mainly a tensile or shear type of stress created either by forces working perpendicular to or parallel to the tooth surface. Shear tests generally produce more true adhesive failures, and thus are preferable for adhesion testing [2].

In vitro evaluations of dentin bonding agents are often made on freshly extracted human teeth, hoping to minimize biochemical changes that occur in the dentin after extraction, but freshly extracted teeth are not frequently available in adequate numbers. Extracted teeth that were collected and stored in disinfecting solution are generally used. These storage solutions include 0.1–1% chloramine, 70% ethanol, 10% formalin, 0.9% saline, 0.05–1% thymol or distilled water. Aquilino *et al.* [3] found storage solutions (0.9% saline, distilled water, 0.05% thymol) did not affect the bond strength of dentinal adhesive/composite to dentin. However, Goddis *et al.* [4] showed bond strengths were affected by storage solutions (70% ethanol, 10% formalin, distilled water with thymol) except for saline. Haller *et al.* [5] suggested that extracted teeth assigned for *in vitro* evaluation of bonding agent should not be stored in 10% formalin, because this reagent anomalously increased the bond strengths.

A factor that contributes significantly to the unreliability of *in vitro* dentin bonding tests systems is the test chemical environment. Intraoral conditions are clearly more complex than those achieved with

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distilled water in the laboratory. As an example, Lee *et al.* [6] reported that the shear bond strength for specimens stored in air was significantly higher than for specimens stored in Moi Stir (Commercial Artificial Saliva). Beech *et al.* [7] reported that elapsed time after extraction can also significantly change bond strengths to dentin, with the magnitudes of these changes depending on the adhesive system used.

The present study was undertaken to evaluate shear bond strengths of modified amalgam-to-dentin interphases, beginning with 10% formaldehyde-treated teeth, to maximize the joint strength from the tooth-side of the interphase. Three dentin bonding systems (Syntac-Variolink, Amalgambond Plus, Amalcoden) and four different storage conditions (100% RH, deionized water, 0.9% NaCl, saliva electrolyte solution) were used prior to testing by the shear failure technique.

2. Materials and methods

Human molars (140) treated with 10% formaldehyde, were used in this study. The enamel on the occlusal surface was removed and the exposed dentin surfaces were ground with 600 grit wet silicon carbide. The teeth were mounted in a plastic holder with a self-curing acrylic resin, for shear testing in a jig. After 24 h storage in deionized water at 37 °C/100% humidity, the prepared teeth were divided into four groups and received the following treatment.

Group 1: the prepared dentinal surfaces of 40 teeth were treated with Syntac-Variolink (Ivoclar, North America, USA) according to the manufacturer's instruction and had a restorative high-copper amalgam (Valiant, Ivoclar North America, USA). This restorative amalgam was condensed against the dentinal surface in a cylindrical plastic mould, 4 mm diameter and 5 mm high. After 24 h storage at 37 °C/100% RH, the specimens were divided into four groups of ten specimens each, and stored for 7 d under one of four different storage conditions (all at 37 °C) : A, 100% relative humidity (RH); B, deionized water (DI water); C, 0.9% NaCl solution; and D, saliva electrolyte solution (Sal-elec).

Group 2: this was the same as group 1, but the prepared dentinal surfaces of 40 teeth were treated with Amalgambond Plus without HPA (High Performance Additive) powder (Parkel, Farmingdale, NY, USA).

Group 3: again, this was the same as group 1, except the prepared dentinal surfaces of 40 teeth were treated with Amalgambond Plus + HPA powder.

Group 4: the prepared dentinal surfaces of 20 teeth were treated with Amalcoden Metal Ionomer Cement (Mion International Corp, Indiana, USA). Amalcoden-treated samples were exposed to conditions A and B only.

After the designated storage time, the mounted specimens were shear tested using an Instron Universal Testing Machine (Series 4200 systems). A chisel-shaped rod was used on the crosshead of the Instron to deliver a shearing force at 0.5 mm min^{-1} that was parallel to the bonding sites and immediately adjacent to the cylinder-shaped amalgam restoration.

ANOVA and Tukey *post hoc* analysis ($P < 0.05$) were performed to evaluate the effects of storage conditions and dentin bonding system on the bond strengths of amalgam-to-dentin interphases.

3. Results

The results of the study are summarized in Table I. In evaluating the effects of storage conditions on bond strengths of amalgam-to-dentin interphases, substantial variations among individual bonded specimens were noted which resulted in the large standard error reported.

For Syntac-Variolink and Amalgambond Plus (without HPA) bonding systems, the analysis of variance indicated no significant differences in bond strengths of amalgam-to-dentin interphases among the four different storage conditions. However, storage condition was a significant variable for Amalgambond Plus + HPA and Amalcoden bonding systems, weaker bond strengths being observed for Amalgambond Plus + HPA in 0.9% NaCl and for Amalcoden in deionized water storage samples.

The bond strengths of Amalgambond Plus + HPA bonded specimens in all storage conditions were the highest (significant at $P < 0.05$). The differences in bond strengths of amalgam-to-dentin specimens made with all bonding systems, when tested from 0.9% NaCl solution, were not significant, however.

4. Discussion

Use of formaldehyde-treated teeth for *in vitro* testing of dentin bonding agents has been controversial, because the bond strength values that result from testing using extracted teeth stored in 10% formaldehyde have exceeded those for the same bonding agents applied to teeth not so-fixed. In this present study, as an example, the bond strengths of amalgam to

TABLE I Interfacial shear strengths (MPa ± S.E.) of amalgam-to-dentin

Adhesive	Condition A 100% RH	Condition B DI water	Condition C 0.9% NaCl	Condition D Sal-elec
Syntac-Variolink	9.96 ± 2.02	7.34 ± 1.66	8.10 ± 1.94	12.01 ± 3.30
Amalgambond Plus	7.14 ± 1.08	5.75 ± 1.40	8.68 ± 1.40	5.33 ± 1.39
AP + HPA	21.50 ± 2.47	14.85 ± 2.34	11.33 ± 1.80	16.21 ± 2.66
Amalcoden	12.09 ± 2.73	2.34 ± 1.18		

formaldehyde-treated teeth were greater than the bond strength values reported by Cao *et al.* [8] and Bagley *et al.* [9], both using freshly extracted teeth.

Aldehydes, such as formaldehyde and glutaraldehyde, are well-known and widely used protein fixatives. In the preparation of specimens for electron microscopy, the fixation effect is based on their cross-linking of proteins by formation of methylene bridges [10]. Strawn *et al.* [11] found there were no shifts in peak position associated with collagen and phosphate when using advanced spectroscopic techniques to monitor chemical change occurring in dentin specimens stored in 10% buffered formalin for up to 28 days. Further, Marshall *et al.* [12] reported no major changes in the mineral phase of the dentin after storage in 10% buffered formalin for periods as long as 4 months.

Sterrett *et al.* [13] observed that formalin treatment of dentin retains a tufted, open collagen structure that offers a greater surface area than other treatment allows. That is, aldehyde-fixed collagen architectures have more interstices for promotion of the conditioner/primers and final bonding resins. The fixed, open collagenous network provides for a degree of mechanical retention through the intermeshing of the tufted fibrils and the treatment materials, so the adhesion of resins to dentin may be mediated mechanically, even in the absence of chemical bonding. Chemical bonds may, of course, form between restorative materials and the organic or inorganic components of dentin, and as is well-known from prior studies, mechanical retention of restorative material is also helped by penetration into dentinal tubules, physically to interlock resin with the dentin surface.

The main research question addressed here is how far the aldehyde fixation effects on improving bond strengths might also extend to the dentin bonding agent systems.

One new system (Syntac adhesive) uses a water solution of 35% polyethyleneglycol dimethacrylate and 5% glutaraldehyde to attach a lightly cured bonding medium containing 60% bisphenol A-glycidyl methacrylate (*bis*-GMA) and 40% triethyleneglycol dimethacrylate (Heliobond), after a primer removes the smear layer and opens the dentinal tubules [5,14]. The glutaraldehyde-based adhesive is applied to dentin prior to application of the bonding agents. It functions to promote resin infiltration into the fixed open dentinal collagen layer, as the glutaraldehyde reacts with the organic part of dentin (collagen) and allows the penetration of the resin composite into the treated dentinal surface, before complete polymerization [15]. A previous system, described by Schumacker *et al.* [16], used *bis*-GMA and triethylene glycol dimethacrylate (TEGDMA) to achieve higher bond strengths than developed by the composite alone, with depth of decalcification and width of the resin-impregnated dentin layer limited to as little as 1 μm [14]. A combination of these advantages, glutaraldehyde fixation plus composite resin, seems necessary effectively to bond amalgam to dentin. Thus, while Retief *et al.* [15] reported that the bond strength of composite resin-to-dentin mediated by Syntac adhesive system was 15.90 ± 2.13 MPa, and Halton *et al.* [17] found the shear bond strength of Syntac adhesive-bonded composite was 13.5 ± 8.6 MPa, much lower bond strengths were observed (0.97 MPa) from Syntac adhesive-bonded amalgam restorations after thermocycling in water [8].

The current study verified this hypothesis, in that bond strength of Syntac-bonded amalgam restoration was significantly improved by the incorporation of Variolink, a dual-curing composite luting cement that contains both *bis*-GMA and TEGDMA as a matrix. Fine particle microhydride fillers are also present in Variolink. It is seen, therefore, that composite resins (like Variolink) specifically enhance the micromechanical retention of the amalgam to dentin having well-preserved aldehyde-fixed open collagen networks, the best results being from a combination of formaldehyde-treated teeth and glutaraldehyde-based adhesives. These bonds are remarkably stable, as witnessed by the bond strengths of the Syntac–Variolink system being invariant in different storage conditions (e.g. saliva electrolyte solution, 0.9% NaCl, deionized water or 100% RH for 7 d at 37 °C).

A remaining issue is that of using strengthening fillers within the composite-enhanced interphase. Amalgambond Plus, a 4META (4-methacryloxyethyl trimellitate anhydrate) bonding system, utilizes a "high performance additive" (HPA) poly methyl methacrylate powder for use with amalgam alloy. Higher bond strength is observed, when the only difference between the original Amalgambond and Amalgambond Plus is the addition of the HPA powder [18]. The current study confirms that, overall, the bond strength values of Amalgambond Plus are significantly higher than the bond strengths of unfilled bonding phases.

This polymer-filler-induced improvement in bond strength is apparently from a "toughening" of the composite interphase exterior to the "hybride layer", which HEMA allows by improving the monomeric diffusivity into the dentin substrate [19, 20].

In this study, the bond strengths of Amalgambond (without HPA) treated specimens stored in deionized water were higher (5.75 ± 1.40 MPa) than that reported by Bagley *et al.* [9] (2.27 ± 0.79 MPa) for restorations of fresh teeth stored for 3 days in deionized water (DI) at room temperature (RT). Cooley *et al.* [21] showed the bond strength of amalgam-to-dentin mediated by Amalgambond was 3.84 ± 1.29 MPa, and Gendusa [22] confirmed that 4-META resin achieves its bond to various surfaces differently with different substrate treatments. It is the formaldehyde treatment of the teeth used in the current study that probably accounts for our increased strengths, even with unfilled Amalgambond.

The significantly increased bond strength values demonstrated by Amalgambond Plus + HPA may have resulted from slower polymerization, allowing more time for the monomers to penetrate the dentinal surface [18], but this explanation does not account for the increased susceptibility of these bonds to underwater deterioration. However, storage conditions were not a significant variable for Amalgambond alone, its dentin–amalgam bonds being extremely stable in all wet environments [22, 23]. The strengths of Amalgambond Plus + HPA bonds to amalgam were diminished by 0.9% NaCl storage solution. There was a significant decrease in bond strength after immersion in 0.9% NaCl solution for 7 d at 37 °C compared to the bond strength of 100% RH/ 37 °C stored specimens. This effect of 0.9% NaCl solution on the bond strength of Amalgambond Plus + HPA bonded specimens may be explained by reference to results with the adhesive luting agent (Amalcoden). Amalcoden also produced bond strengths for amalgam-to-dentin comparable to those using the dentin bonding agents (Syntac-Variolink and Amalgambond Plus without HPA) when the specimens were challenged only by storage at 100% RH/37 °C, before shear testing.

Ionomer cements like Amalcoden consist of a filler powder form of silicate glass and an aqueous solution of high molecular weight polyacrylic acids. When the two components are mixed in a predetermined proportion, a solid mass forms as a result of the reaction between the leachable compounds of glass and the polyacrylic acid. During the early stage of the reaction, water serves as the medium. The latter part of the setting process includes further cross-linking of polyacrylic chains by metallic ions and hydration of the hydrogel salt by the same water medium. Owing to this hydration, the glass ionomer cement exhibits an increase in strength over a long period of time. So it is possible to explain why the bond strength of Amalcoden is comparable to the bond strength of Syntac-Variolink and Amalgambond bonding agent from the specimens stored at 100% RH.

Ionomer amalgam bonding cements exposed to aggressive, continuous hydration, moreover, lose their unique physical and chemical bonds between metal and tooth structure, allowing penetration of boundary layers, and diminished interface protection once the margins begin to be soluble.

In this study, the bond strength of Amalcoden-treated specimens immersed in deionized water for 7 d at 37 °C were significantly lower than for specimens stored at 100% RH. The bond strength value reported in this study (2.34 ± 1.18 MPa) was lower than that reported by Covey and Moon [24] (3.26 MPa) for the same storage conditions, despite the intrinsic advantage in our study provided by formaldehyde pretreatment of the tooth. It is likely, therefore, that the breakdown was in the particle-filled cement phase of this bond, analogous to the failure of the particle-filled Amalgambond Plus.

Oilo [25] noted that biodegradation of cements is a complex process of absorption, disintegration and outward transportation of ions. Shen and Grimaudo [26] reported that glass ionomer cement must be protected from direct water contact as long as possible, in order to reach an acceptable level of strength, and this conclusion also seems applicable to polymer-filled resins.

5. Conclusion

It is found that stabilization of the entire interphase is important to strength development and retention in dentin-to-amalgam bonding. Improvement of restorative-to-dentin interfaces can result from aldehyde pretreatment of teeth, use of glutaraldehyde-based adhesives, use of *bis*-GMA and TEGDMA resins, and possibly incorporation of powder fillers. The influence of storage conditions on the bond strengths of the filled systems needs further investigation.

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