DENTAL TECHNOLOGY

Long-term durability of adhesive systems bonded to fresh amalgam

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A strong durable resin bond to fresh amalgam is desired in composite-veneered amalgam restorations and in adhesive amalgam restorations. The purpose of this study was to evaluate the influence of long-term water storage on the durability of the shear bond strength of new adhesive systems bonded to fresh amalgam. Sixty cylindrical specimens composed of equal parts of amalgam and composite, with a layer of bonding material in between, were prepared for each adhesive system: All-Bond 2, Amalgambond Plus, High-Q-Bond, and Comspan. Specimens were divided into three subgroups and immersed in saline at 37°C for either 48 hours, 3 months, or 6 months. After the immersion period, specimens were thermocycled and subjected to shear bond strength testing. Shear bond strength of Comspan and High-Q-Bond adhesives did not deteriorate significantly during the 6-month experiment and maintained a mostly mixed mode of failure. All-Bond 2 and Amalgambond Plus adhesives exhibited deterioration of the shear bond strength as a function of immersion time and shifted from dominantly mixed mode of failure to totally adhesive (All-Bond 2) or mostly adhesive failure (Amalgambond Plus). Incubation in saline for long periods should be a standard test in evaluating the bond of new adhesive systems to fresh amalgam, whereas short exposure time to water might be misleading. (J Prosthet Dent 1996;76:431-6.)

Composite-veneered amalgam restoration is a method of treatment primarily aimed at the visible areas in the mouth, incorporating both the desired mechanical properties of amalgam and the esthetic qualities of composites.[1-3] This procedure can be accomplished in one or two sessions. In the one-session procedure, retention is obtained from freshly mixed amalgam immediately after condensation. In the two-session procedure, retention is obtained from set amalgam. Retention can be provided by mechanical and/or micromechanical means[1,4] or chemical means.[5] For chemical means, multipurpose adhesive materials are used that bond to amalgam, composite, and tooth structures.

Previous studies have focused on bonding systems that adhere composites to set amalgam. Systems that include bonding resins such as 4-methacryloxy ethyl trimellitate anhydride (4-META), biphenyldimethacrylate (BPDM), or phosphonated cement of the Bis-GMA type yield shear bond strength (SBS) values that range from 3.19 to 7.47 MPa,[5,6] up to 12.9 MPa.[7] Bonding systems identical to those mentioned previously yielded SBS of composite to fresh amalgam within the range of 3.45 to 5.19 MPa[8] and tensile strength of 6.74 MPa.[9]

These SBS values between fresh or set amalgam and composites are identical to those reported for freshly mixed amalgam and dentin: 3.84 to 5.10 MPa,[10-12] up to 11.0 to 13.0 MPa.[7,13] The common denominator to amalgam-composite system or amalgam-dentin system that impairs the bond strength is the bond between the adhesive material and the amalgam. The existence of a "true" chemical bond between amalgam and adhesive resins was not verified. Micromechanical retention is now considered the most likely mechanism of resin-amalgam bonding.[14,15]

A strong, durable resin bond to fresh amalgam is desired in composite-veneered amalgam restorations and in adhesive amalgam restorations. Previous studies that evaluated SBS of composites to amalgam by multipurpose adhesive materials did not examine the impact of prolonged aging in water. Hydrolysis of systems that contain either 4-META[16,17] or 10-methacryloxydecyl dihydrogen-phosphate (10-MDP)[18] and involve resin-dentin interface was previously reported. A significant decrease in bond strength over storage time was also reported for composite bonded to NiCr alloy by MDP-containing adhesive resin.[19] The possible impairment of resin-amalgam interface after long-term immersion in water should thus be considered.

The purpose of this study was to evaluate the influence of long-term water storage on the durability of the shear bond strength of adhesive systems bonded to fresh amalgam.

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Table I. Adhesive systems examined (composition and procedures)

Adhesive system	Composition	Lot No.	Procedure
All-Bond 2	Primer A	099103	Mix Primer A & B, apply
(Bisco, Itasca, Ill.)	Primer B	089163	2 coats, dry for 5 seconds
	Dual Cure Opaquer:		Mix Opaquer Base and
	Base	099013	Catalyst, apply, light cure
	Accelerator	089033	for 10 seconds
	Dentin/Enamel	099303	Brush a thin layer, light cure
	Bonding Resin		for 20 seconds
Amalgambond Plus	Adhesive agent	41932	Brush a thin layer, air dry,
(Parkell,			leave undisturbed for 30
Farmingdale, NY)			seconds
	Base B	30602	3 drops Base, 1 drop
	Catalyst C	307041	Catalyst, 1 scoop HPA;
	HPA Additive	36691	stir gently, apply a thin
			layer, let dry for 60 seconds
High -Q-Bond	Primer C	709064	Apply without drying
(BJM Laboratory,	Chemical Activator A	709054	Mix 4 drops of A with the
Givatayim, Israel)	Base B	709054	powder content of B, apply
			thin even layer
Comspan	Bonding agent	930101	Stir Base and Catalyst for 5
(LD Caulk, Milford,			seconds and apply
Delaware)	Opaque	9304011	Mix Base and Catalyst for
			20 seconds and apply

MATERIAL AND METHODS

Sixty cylindrical specimens, 6 mm high × 6 mm in diameter, composed of equal parts of amalgam and composite with a layer of bonding material in between, were prepared for each adhesive system. The name of the adhesive systems, manufacturers, lot numbers, composition, and procedures are presented in Table I.

Cylindrical Teflon (Du Pont Co., Wilmington, Del.) molds with an inner dimensions of 6 mm × 6 mm were fabricated. A close fitting Perspex (Austenal Dental Products, Ltd., Harrow, England) piston, 6 mm × 3 mm, was matched to each hole in the Teflon mold to create a cavity with dimensions of 6 mm × 3 mm (Fig. 1, *A*). A high-copper amalgam (Oralloy, Coltene-Whaledent, Mahwah, N. J.) was condensed against the Perspex piston by use of an automatic condensor (Kavo-Biberach-Ris, Germany), leaving the amalgam surface continuous with the Teflon cylinder surface (Fig. 1, *B*). The mold was reversed and the piston was gently released. Each adhesive system was carefully prepared and applied, according to the manufacturer's recommended steps, to the freshly condensed amalgam surface (Table I). A composite (Brilliant A2, Coltene, Altstatten, Switzerland) was packed against the layer of the bonding agent in two increments. Each increment was cured for 60 seconds at a 90-degree angle to the surface of the composite with a visible light–curing unit (Demetron 401, Demetron Research Corp., Danbury, Conn.). The intensity of the curing light was monitored periodically with a curing radiometer (Demetron Research Corp.) and its intensity was consistently in the range of 450 to 500 mW/cm^2. Excess composite was removed before final curing to ensure a continuous surface with the Teflon mold (Fig. 1, *C*).

Specimens were gently released from the mold, carefully inspected to rule out possible defects such as voids, and stored at 37° C and 100% humidity in a lightproof container for 1 week. The specimens were then divided into three subgroups: 20 specimens were immersed in saline at 37° C for 48 hours; 20 specimens were immersed in similar conditions for 3 months; and 20 specimens were immersed in similar conditions for 6 months. The aqueous medium was refreshed every week.

After the immersion period, specimens were thermocycled for 500 cycles at 5° and 55° C, with a dwell time of 20 seconds by use of a constant temperature bath (Techne Inc., Princeton, N. J.).

Shear bond strength testing

A device constructed from two identical 3 mm thick stainless steel plates with a 6 mm diameter penetrating cylindrical hole was fabricated. By combining the plates, a testing chamber was created in which the samples fit exactly. The device was attached to the Universal testing machine (Instron Corp., Canton, Mass.) with a 50 kg load cell. The device was subjected to a continuously increasing tensile force with a crosshead speed of 1 mm/minute until debonding resulted. By this method a shearing plane was created exactly in the amalgam-composite interface. The force at which debonding occurred was recorded on a strip chart and SBS (MPa) was calculated from the cross-sectional region of the specimen.

Microscopic evaluation

Each debonded specimen was examined with a stereomicroscope (Wild M8, Wild Heerbrugg, Heerbrugg, Switzerland) at ×30 magnification so that the type of failure could be evaluated. Because all the debonded composite surfaces were completely covered by adhesive resin, failure analysis was performed on the debonded amalgam disk. The mode of failure was determined to be either adhesive (locus of failure in the adhesive/amalgam interface), cohesive (locus of failure within the adhesive), or mixed in which adhesive resin was partially bonded to the amalgam.

Statistical analysis

Bond strength data were subjected to a two-way analysis of variance (ANOVA). When the F-ratios were significant, the Bonferroni multiple comparisons test was used to compare specific means at $p<0.05$. The statistical data were processed with the BMDP software system (University of California, Berkeley, Calif.).

RESULTS

The mean shear bond strengths (SBS) and standard deviations (SD) for each group are illustrated in Figure 2. Two-way ANOVA revealed significant differences in bond strength based on adhesive materials and immersion times and their interaction (Table II). Bonferroni's multiple comparisons test was used to test the significant differences between specific means (Fig. 3). SBS provided by the four adhesive systems after 48 hours did not differ significantly. All-Bond 2 and Amalgambond Plus adhesives exhibited deterioration of the shear bond strength as a function of immersion time: All-Bond 2 adhesive deteriorated after 3 months, and Amalgambond Plus adhesive after 6 months. The greatest deterioration in bond strength was observed for All-Bond 2: 70% after 3 months and 95% after 6 months. To rule out any possible effect of the specific batch of All-Bond 2 used, the experiment was repeated with another batch (No. 109163) with similar results.

Shear bond strength of Comspan and High-Q-Bond adhesives did not deteriorate significantly during the 6-month experiment. High-Q-Bond adhesive exhibited superior results at all stages of the experiment, with statistically significant difference after 3 and 6 months (Fig. 3).

Table III specifies the modes of failure as determined by optical microscopy for all adhesive systems at different immersion times. As the debonded composite disks were completely covered by adhesive resin at all experimental stages, the mode of failure refers to the amalgam disks-adhesive resin interface. High-Q-Bond adhesive demonstrated mainly cohesive or mixed mode of failure at all experimental stages. Comspan adhesive exhibited mostly mixed mode of failure in all tested conditions. All-Bond 2 adhesive changed the mode of failure from less adhesive after 48 hours to more adhesive after 3 months, and lastly to totally adhesive after 6 months. Amalgambond Plus adhesive shifted from less to more adhesive type of failure only from 3 to 6 months.

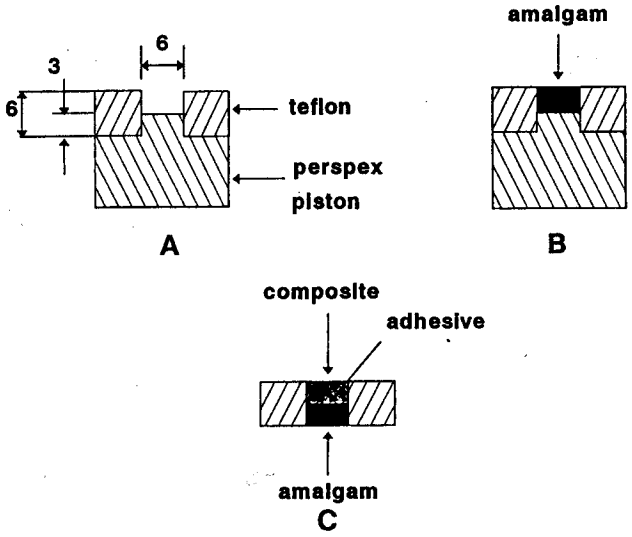

Fig. 1. Stages of sample preparation. (*A*) Teflon mold and perspex piston. (*B*) Postcondensation stage. (*C*) Final specimen within mold.

DISCUSSION

Clinical situations for placing composite resin adjacent to existing or freshly placed amalgam have been described.[1,3,20-23] Mechanical and/or micromechanical means that provide retention include roughening the amalgam, preparing mechanical undercuts, direct bonding of composite to etched enamel around the amalgam,[24,25] or inserting self-threading pins into the set amalgam.[1] The application of an adhesive system on the amalgam surface before placing composite has the advantages of avoiding aggressive mechanical means that compromise the amalgam restoration, providing extra retention, and decreasing microleakage at the junction of amalgam alloy and composite resin.[6,22]

Macromechanical means (undercuts, self-threading pins) or surface finishing (diamond burs, microsandblasting) are inappropriate to apply on fresh amalgam immediately after condensation, to obtain retention. Thus, retention to fresh amalgam is more dependent on the application of adhesives. The adhesive systems used in this study yielded SBS, 48 hours after immersion in the range of 4.05 to 6.31 MPa without statistically significant differences ($p>0.05$). These values do not necessarily designate the ultimate shear strength of the bond. Other factors should be considered such as (1) the influence of the type of amalgam substrate[26]; (2) tensile stress induced by a bending moment instead of by shear stresses[27] in a non-pure shear state of stresses; and (3) film thickness of the adhesive not controlled, although the manufacturer's instructions

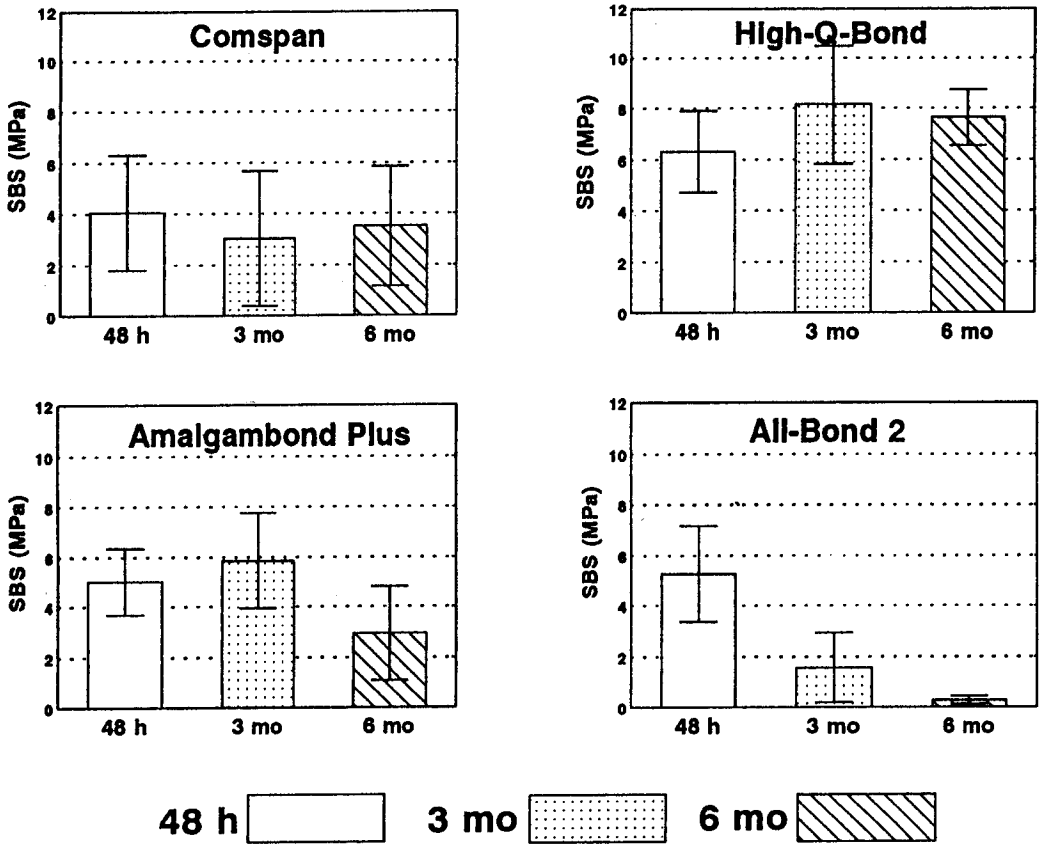

Fig. 2. Mean shear bond strength and standard deviation for different adhesive systems at 48-hour, 3-month, and 6-month immersion periods.

Table II. Two-way analysis of variance

Source of Variation	Sum of Squares	DF	Mean Square	F-Ratio	F-Prob
Adhesive system	821.572	3	273.857	79.40	0.0001
Immersion time	102.413	2	51.207	14.85	0.0001
Interaction	302.146	6	50.357	14.60	0.0001
Error	786.362	228	3.449		

Table III. Mode of failure

Adhesive material	Storage time	No.	Cohesive	Mixed	Adhesive
Comspan		60	11	30	19
	48 hours	20	5	7	8
	3 months	20	2	12	6
	6 months	20	4	11	5
All-Bond 2		60	6	13	41
	48 hours	20	5	8	7
	3 months	20	1	5	14
	6 months	20	0	0	20
Amalgambond Plus		60	8	24	28
	48 hours	20	3	10	7
	3 months	20	4	8	8
	6 months	20	1	6	13
High-Q-Bond		60	21	30	9
	48 hours	20	7	10	3
	3 months	20	9	9	2
	6 months	20	5	11	4

were carefully followed. Comparable values of 3.45 to 5.19 MPa without a statistically significant difference obtained with All-Bond, Clearfil-New Bond, and Amalgambond adhesives were reported by Bichacho et al.[8] Miller et al.[15] demonstrated a significantly weaker bond for fresh amalgam alloy placed directly onto dentin wetted by Amalgambond adhesive compared with set amalgam adhered to the same treated dentin. The larger surface area after surface finishing procedures were applied and the absence of unreacted mercury from the wet amalgam enabled greater microscopic mechanical interlocking to occur onto set amalgam compared with fresh amalgam.[15]

Specimens of composite bonded to amalgam are routinely incubated in physiologic saline before debonding procedures. The common storage time is 24 hours.[6,11,12] An observation of a significant decrease in SBS after a long period of water immersion was demonstrated in this study and was dependent on the specific adhesive studied. Amalgambond Plus adhesive did not deteriorate during the 3 months, but decreased a statistically significant amount over 6 months. All-Bond 2 adhesive deteriorated progressively after 3 and 6 months, whereas High-Q-Bond and Comspan adhesives did not deteriorate significantly during the 6-month experiment.

Postcuring processes and heat effects act toward improving the mechanical properties of the adhesives.[28,29] These outcomes are adversely affected simply by water filling voids within the molecular structure of the matrix or causing the sample to swell, concomitantly with degradation of filler-matrix interfaces.[30,31] Long exposure time to water is thus needed for the aging phenomena to become dominant, whereas short exposure experiments might be misleading. Diaz-Arnold et al.[32] measured the water sorption of composite adhesives such as Comspan by near infrared spectroscopy and demonstrated rapid initial water uptake within the first 2 weeks of storage, a gradual increase up to 4 months, and a minimal gain afterwards. A true equilibrium was not reached even after 1 year.

Indications of the possible role of water after long-term immersion periods with the currently investigated adhesives come from bond strength studies involving adhesive–dentin interface and microleakage tests. Recent studies report that the tensile bond strength to extracted bovine dentin with 4-META/MMA-TBB resin decreased remarkably after storage in water for 1 or more years.[16,17,33] Although bonded amalgam techniques initially prevented leakage, there appeared to be an increase in leakage at 6 months, especially at the root surface margins, and the complete inability to significantly reduce microleakage after 1 year.[34]

The mode of failure in this investigation was either cohesive, adhesive, or mixed mode. A fully cohesive failure of the adhesive implied 100% coverage of both composite and amalgam debonded surfaces. No cohesive failure within amalgam or composite was noted. Such analysis of failure has several disadvantages and therefore must be referred to qualitatively. Because failure occurs at the atomic level, it is not possible to determine whether the failure is truly adhesive or cohesive by using light microscopy only. An adhesive failure could still have a few monolayers of the adhesive material bonded to the surface, whereas the microscopic evaluation would "see through" that layer and misinterpret the bond failure. The term "mixed mode" is not illustrative enough because it does not determine what percentage of the debonded amalgam disk is covered with the adhesive.

Adhesive	48 hours	3 months	6 months
Comspan	4.05 (2.25)	3.03 (2.65)	3.51 (2.35)
All-Bond 2	5.27 (1.90)	1.57 (1.37)	0.28 (0.16)
Amalgambond Plus	5.02 (1.34)	5.85 (1.91)	2.95 (1.86)
High-Q-Bond	6.31 (1.59)	8.16 (2.33)	7.63 (1.10)

Horizontal or vertical lines in the same plane designate statistically homogenous groups ($p > 0.05$). Groups not connected by horizontal or vertical lines in the same plane are statistically significantly different ($p < 0.05$).

Fig. 3. Bonferroni's multiple comparisons test of shear bond strength. Mean (SD) in MPa.

Comspan and High-Q-Bond adhesives maintained mostly a mixed mode of failure throughout the 6-month experiment, concomitant with no deterioration of the SBS values. All-Bond 2 and Amalgambond Plus adhesives shifted from initially a dominantly mixed mode of failure to totally adhesive (All-Bond 2) or mostly adhesive (Amalgambond Plus), concomitant with deterioration in the SBS values. In spite of the mentioned disadvantages, the mode of failure of the adhesives studied correlated with the SBS values. Adhesives maintaining good durability do not change the mode of failure, whereas adhesives maintaining poor durability of the SBS values shift toward adhesive mode of failure. Postulated mechanisms of the interaction with water are either washing away or hydrolysis of the composite.

Because some adhesive systems bonded to fresh amalgam are undergoing severe deterioration in SBS values concomitant with shifting mode of failure towards dominantly adhesive type, incubation in saline for long periods should be a standard test for evaluating new materials, whereas short exposure time to water might be misleading.

SUMMARY

1. All-Bond 2, Amalgambond Plus, High-Q-Bond, and Comspan adhesive systems initially provided similar SBS between fresh amalgam and composite.

2. High-Q-Bond and Comspan adhesives maintained substantive durability and did not change the mode of

failure. All-Bond 2 and Amalgambond Plus adhesives maintained SBS values that exhibited poor durability during the 6 months and shifted toward adhesive mode of failure.

3. Testing SBS values to fresh amalgam after short exposure time to saline might be misleading.

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