THE LONG TERM DURABILITY OF BOND STRENGTHS TO DENTIN

BY

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Abstract

The aim of this study was to investigate the durability, throughout one year, of tensile bond strengths (TBS) to bovine dentin using various commercial and experimental bonding systems.

Specimens were stored in a controlled solution of ion-exchanged water containing plaster chips and sodium azide.

From the results it was concluded that the changes in TBS were not uniform over time, but a significant decrease was usually observed. For Super Bond D-liner and KB-100, the TBS were the highest and exhibited remarkable stability over the test period.

The mode of fracture was noted to vary depending on the treatment system used, and was independent of TBS. Generally, the fracture mode tended to show increases in adhesive/cohesive failures within the resin over time. Super Bond D-liner always exhibited adhesive type failure at the tooth interface, and later involved failure in the hybrid layer. KB-100 showed very little change in failure over one year, being usually adhesive between bonding resin and resin composite.

The results from this study indicate the need to carry out durability studies for the basic evaluation of all bonding systems. It was shown that the use of a controlled storage solution is important.

Introduction

Since the advent of bonding to enamel by the use of phosphoric acid (Buonocore [1]), and slightly later the unsuccessful application to dentin (Buonocore [2]) of an experimental bonding agent, great changes have occurred in adhesive dentistry. Enamel bonding is now a widely accepted restorative method, and likewise dentin bonding is now gaining much wider popularity. This acceptance of dentin bonding has been brought about initially by the efforts of Fusayama [3] with his technique of total etching and the use of a dentin compatible bonding agent (Clearfil Bond F). Since that time, the creation of many new materials has come about associated with several changes in the philosophy related to the need for using strong acidic solutions such as 37% phosphoric acid for conditioning. Recently the newest dentin bonding systems such as Liner Bond, All Bond, Scotchbond Multi-Purpose, and Super Bond D-liner have incorporated milder acidic conditioning agents such as 10–20 Ca (10% citric acid containing 20% calcium chloride), 10%

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phosphoric acid, maleic acid, and 10–3 solution (10% citric acid containing 3% ferric chloride). Associated with these conditioners, these bonding systems incorporate priming agents which are believed to promote the penetration of the bonding resin into the conditioned dentin surface, as well as cause an alteration in the arrangement and perhaps structure of the exposed decalcified collagen fibers (Sugizaki [4]). Generally, the mechanism of these new systems is to remove or modify the smear layer by acidic conditioning, and 'prime' the altered dentin to increase the wetting ability and infiltration of the bonding resin into the dentin surface, which results in a resin-impregnated layer. More recently an experimental system has been tested which combines the conditioning-priming function into one step. This system also creates a very thin resin-impregnated layer, thus ensuring that minimal damage to the dentin will occur (Hosoda *et al.* [5]). A further feature of this new system is the fact that the smear layer is not removed like those systems which etch, then wash with a strong air-water spray.

The evaluation of dentin bonding systems is usually carried out *in vitro* initially to determine the tensile or shear bond strength. However, the tests are usually limited to 24-hour bond strength results. Although these evaluation methods are most adequate for determining the adhesive strength of the material, they do not provide any information about the durability of the material from a long term viewpoint. Most often durability testing is performed by the use of either thermal cycling or load stress. This can be regarded as a means of accelerated ageing of the bonding system, a little similar to that proposed by Asmussen [6] for ageing of resin composites at 60°C. One question raised by the MD-156 Task Group

(Soderholm [7]) was concerned with bond durability over the long term from the aspect of "weathering". It is still unclear what the hydrolytic effects of water are on dentin bonding systems, and it was stated that current knowledge is still at a "very primitive level" (Soderholm [7]). The above-mentioned 'durability' tests still only address bond durability in the short term. From the long term situation little information has so far been obtained, or published, regarding bond stability of resin systems for periods of one or more years. To date only one study with Super Bond (4 META-MMA/TBB) has been published investigating five-year bond strengths (Kiyomura [8]). Other studies by Chan *et al.* [9], Fasbinder *et al.* [10], and Tjan *et al.* [11] have investigated the six-month or one-year bond strengths of such systems as Scotchbond, Bondlite, Gluma system, New Bond, Clearfil Photobond, Tenure, *etc.*

The purpose of this study was to investigate the durability of tensile bond strength (TBS) using various methods of tooth surface treatment throughout the period of one year when stored in calcium-enriched ion-exchanged water. In addition, the modes of tensile fracture were observed in detail.

MATERIALS AND METHODS

The materials used, the probable composition and manufacturers are listed in Table 1. Bovine teeth stored frozen soon after extraction were used for this study. Flat surfaces in superficial dentin were prepared on a model grinder and finished with 600-grit silicon carbide paper under running water. The roots of the teeth were removed to a location approximately 2 mm below the cemento-enamel junction.

The bonding surface was covered with a piece of double-sided adhesive tape in which a 4-mm diameter hole had been cut

Table 1. Materials, Composition, Batch Nos., and Manufacturers

Conditioner	Composition	Batch Number	Manufacturer
K-etchant	37% phosphoric acid	064	Kuraray Co., Osaka, Japan
Ca agent	10% citric acid in 20% calcium chloride (10–20 Ca)	TST-001	Kuraray Co., Osaka, Japan
10-3 solution	10%citric acid in 3% ferric chloride	10702	Sun Medical Co., Kyoto, Japan
KB-100	phenyl-P, NMSA* HEMA†, additional compounds	B-2-1-01 B-2-2-01	Kuraray Co., Japan
Primer			
SA primer	NMSA*	TSA-001	Kuraray Co., Japan
Gluma primer	35% HEMA† in 5% aq. glutaraldehyde	0080F	Bayer Japan, Osaka, Japan
Super Bond D-liner Primer	35% aq. HEMA†	10701	Sun Medical Co., Japan
Bonding Resin			
Clearfil Photo Bond	Uni: Bis-GMA, HEMA†, 10-MDP§ Cat: Aromatic compounds	Uni: 236 Cat: 107	Kuraray Co., Japan
Super Bond D-liner	Liq: 4 META, MMA, 2.6E¶ Cat: tri-butyl borane	Liq: 10702 Cat: 108032	Sun Medical Co., Japan
KB-100	Bis-GMA, filler particles	TIBOR 12201	Kuraray Co., Japan
Protect Liner	Bis-GMA, filler particles	TRTL-101	Kuraray Co., Japan
Photo Clearfil Bright	Shade XL	7304	Kuraray Co., Japan

*3% N-methacryloyl 5-aminosalicylic acid in 80% ethanol
†2-hydroxyethyl methacrylate
§10-methacryloyloxydecyl dihydrogen phosphate
¶2,2-Bis [4-(methacryloxy polyethoxy) phenyl] propane

to delineate the bonding area. On top of the adhesive tape, a 1-mm thick plastic washer, of a diameter slightly greater than 4 mm, was attached as a spacer for the placement of resin composite.

Then the teeth were conditioned and/or primed according to the groups listed in Table 2. The conditioner was placed for 40 s, except for Group SD in which the solution was left for 15 s. The short conditioning time for Group SD was performed because the manufacturer recommends a much shorter conditioning period. After this, the teeth were washed with an air-water spray for approximately 10 s, and then dried with oil-free compressed air for a further 10–15 s. The priming solution was then placed for 60 s and air-dried until the solution had evaporated. For group KB only the conditioner,

Table 2. Group Codes and Treatment Methods for Bonding

Group	Conditioner (40s)	Primer (60s)	Bonding resin	Protect Liner
K	K-etchant	—	Photobond	—
KS	⁁	SA primer	⁁	—
KG	⁁	Gluma primer	⁁	—
KP	⁁	—	⁁	+
KSP	⁁	SA primer	⁁	+
C	Ca agent	—	⁁	—
CS	⁁	SA primer	⁁	—
CG	⁁	Gluma primer	⁁	—
CP	⁁	—	⁁	+
LB	⁁	SA primer	⁁	+
KB	KB conditioner	—	KB bonding agent	—
SD	10-3 solution (15s)	HEMA	D-liner	—

which also played the role of the primer, was placed on the tooth for 40 s, then air-dried gently until the solution produced a "tacky" appearance, or the treated surface appeared shiny. In all groups after priming, the bonding resin was placed and light-cured for 20 s, except Super Bond D-liner which was self-cured. Over the bonding resin, the restorative resin composite was placed and light-cured for a further 40 s. In the groups where Protect Liner was placed, this was carried out after curing of the bonding resin. The Protect Liner was light-cured for a period of 20 s. The resin composite was covered with a plastic matrix strip and glass slide to create a flat surface before it was light cured. Following completion of the bonding agent and resin composite placement, the pulps of the teeth were removed where possible. The teeth were then placed in plastic containers containing 100 ml of ion-exchanged water (Yamato Autostill WG-25), 0.4% sodium azide (NaN_3), and two pieces of plaster of Paris measuring $12 \times 7 \times 2$ mm thick. Ten teeth were tested for each group at each time period, except for Group KB at the one- and three-month time periods, where only nine teeth were

used. The teeth were stored in the solution undisturbed at 37°C for periods of 24 hours, one, three, six and 12 months prior to testing.

One day before testing for the tensile bond strengths (TBS), the containers were removed from the incubator to cool to room temperature. Following this the pH of the storage water was determined, then the teeth were washed and the storage solution was replaced with tap water before cementation of stainless-steel rods to be used in the TBS test.

Prior to cementation of the stainless-steel rods, the water-damaged surface of the resin composite was removed by wet-grinding with 280-grit silicon carbide paper, acid etched with 37% phosphoric acid for 120 s, then washed and dried with oil free compressed air. The cleaned surface was then treated with Clearfil Photo Bond to which was added Clearfil Porcelain Bond Activator (Kuraray Co., Osaka, Japan) and light-cured for 10 s. The stainless-steel rods were cemented perpendicularly with an adhesive resin cement (Panavia EX, Kuraray Co., Osaka, Japan) to the treated surfaces. After setting of the cement, the teeth were placed in water at

room temperature until the TBS test approximately 24 hours later. The 24-hour test specimens were, however, stored at 37°C.

The TBS test was carried out using a universal type testing machine (AG-500B, Shimadzu Co., Tokyo, Japan) with a cross-head speed of 2 mm/min.

After the TBS test, all specimens were visually examined to determine the mode of tensile failure. Each specimen was classified into one of four categories as represented in Fig. 1. From these specimens, typical examples were selected for observation under SEM.

Preparation of the specimens for SEM observation was carried out as follows: the teeth were initially sectioned using a slow-speed diamond saw under water spray (Bronwill Co. Ltd., Rochester N.Y., U.S.A.) so that only the fractured bonding surface remained. After this, the surface was gold sputter-coated and then observed by the SEM (JXA-840, JEOL Co., Tokyo, Japan).

The results of the TBS test were statistically analyzed using ANOVA and Duncan's Multiple Range Test.

RESULTS

The results of the TBS for each group are listed in Table 3. Figs. 2–4 illustrate the mode of fracture exhibited for each group as time varied. The variation of pH is shown in Table 4. A description of the statistical analysis and results obtained for each listed group are as follows:

Group K: This group showed relatively low, but stable TBS for the first six months, and then a marked decrease at 12 months. The mode of failure was always adhesive throughout the whole test period (Fig. 2). The pH of the solutions ranged from pH 7.6 at one month to pH 7.1 at three and six months. (The values at 24 hours and one year were not recorded.) Statistically the one-year results were significantly lower than all other time periods ($p < 0.05$). The results at one day were not statistically different when compared with the three- and six-month results, but were significant when compared with the one-month result ($p < 0.05$).

Group KS: An increase in the TBS was noted in this group which utilizes SA primer. However, by one year the results were significantly lower than the one-day results ($p < 0.01$). On comparison, all other time periods were not significantly different. The variation in pH was also quite small, the highest was pH 7.4 at three and six months, the other time periods that were tested registered a pH of 7.1. Fig. 2 shows that there was a steady increase in the number of adhesive failures over the one-year period, and a decrease in the number of cohesive failures of dentin.
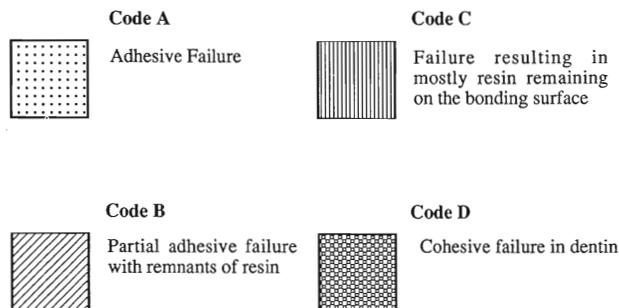
Group KG: This group showed a very

Code A

Adhesive Failure

Code C

Failure resulting in mostly resin remaining on the bonding surface

Code B

Partial adhesive failure with remnants of resin

Code D

Cohesive failure in dentin

Fig. 1 Code groupings used for determining the mode of fracture.

MICHAEL F. BURROW, *et al.*

Table 3. Tensile Bond Strengths (MPa) Mean±SD, and [Range]

Group	1 day	1 month	3 months	6 months	12 months
K	6.7±1.9 [4.4–10.0]	5.0±1.4 [3.6–7.4]	5.9±1.6 [3.9–7.0]	6.0±1.1 [4.8–7.8]	3.8±0.7 [2.4–4.9]
KS	9.3±1.8 [6.6–12.1]	8.6±2.0 [5.8–11.4]	7.6±2.2 [5.1–11.8]	8.5±1.9 [6.4–11.6]	6.9±1.7 [4.9–9.0]
KG	13.2±2.0 [9.1–17.8]	8.9±2.2 [6.6–14.5]	7.7±2.3 [5.0–12.6]	8.8±1.6 [7.3–13.0]	9.9±2.4 [7.0–14.0]
KP	5.2±1.4 [3.5–7.6]	5.8±1.3 [4.1–9.2]	4.1±1.2 [2.9–6.6]	7.6±1.1 [6.0–9.7]	4.5±1.4 [3.0–6.8]
KSP	10.6±2.8 [6.7–15.0]	9.2±3.1 [6.6–15.1]	8.5±1.6 [6.0–12.4]	10.5±1.6 [7.9–12.7]	10.2±1.6 [8.5–13.7]
C	8.2±2.0 [6.0–11.3]	7.2±2.5 [3.8–12.1]	5.1±0.9 [3.6–6.3]	5.1±1.1 [3.6–6.5]	4.4±0.7 [3.2–6.0]
CS	13.3±1.9 [10.5–17.6]	9.6±2.9 [6.0–15.4]	6.4±2.0 [3.5–9.6]	8.0±1.9 [6.0–11.9]	7.3±0.9 [6.1–9.7]
CG	11.9±2.1 [9.0–16.4]	10.5±4.1 [6.0–21.0]	8.5±1.9 [6.0–12.1]	7.4±1.4 [5.4–9.2]	9.0±2.1 [5.9–11.8]
CP	7.7±1.5 [5.5–10.5]	6.3±1.6 [2.9–8.5]	5.9±2.4 [3.1–9.4]	5.7±0.7 [4.4–6.5]	5.5±0.8 [4.6–6.9]
LB	13.4±2.3 [10.0–16.5]	10.8±2.4 [7.3–15.7]	8.2±1.9 [4.6–11.9]	7.0±1.5 [5.1–10.3]	6.9±0.9 [4.9–8.4]
KB	13.2±2.9 [9.3–18.9]	12.8±4.3 [8.1–21.8]	13.4±4.0 [9.6–18.9]	14.0±2.8 [9.4–21.6]	13.1±3.0 [9.0–19.2]
SD	15.1±2.9 [10.0–20.2]	18.4±4.2 [14.0–27.3]	13.8±3.8 [8.0–21.0]	12.3±3.2 [9.1–19.2]	13.3±2.4 [9.9–16.7]

high TBS at one day with a statistically significant drop in TBS over the first month (p<0.01). From the period of one month onwards the TBS remained quite stable. The pH variation of the storage solution was also quite small, ranging from pH 7.6 at one-month to pH 7.0 at the three-month period. The fracture mode of the specimens did not change throughout the test period, and always showed the vast majority involving cohesive failure of dentin.

Group KP: This group showed very little difference in TBS when compared with the results of Group K, except that there was a large variation of TBS for all test times. The result at six months was significantly higher than all other time periods in this group (p<0.01). There was no statistical variation between the results at all the other time periods indicating this group was very stable in TBS. Fracture mode also showed very little variation, with the bulk being adhesive in nature. At the
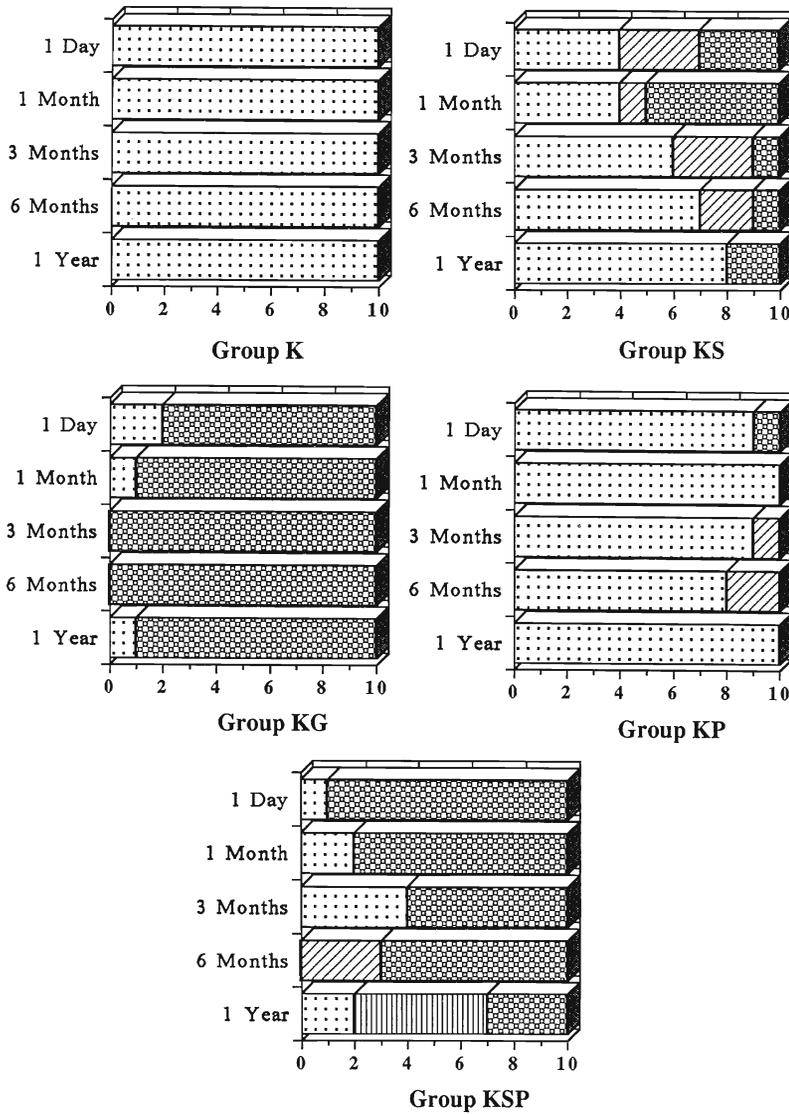
Fig. 2 Fracture mode of groups conditioned with K-etchant.

three- and six-month periods there was a slight increase in partial adhesive failure with remnants of resin remaining on the tooth surface. The pH values of the solutions over the various times were also very stable.

Group KSP: In this group, the pH values of the storage solutions also varied little, being highest at three months (pH 7.4) and lowest at six months (pH 7.0). The

TBS results for this group are similar to group KS although more stable. Significant differences were seen between the three-month and six-month, three-month and one-year periods, but all other comparisons were not statistically significantly different (p<0.05). In fact, the TBS at one day and one year were almost exactly the same. However, fracture mode changed over the test period. The modes up to six
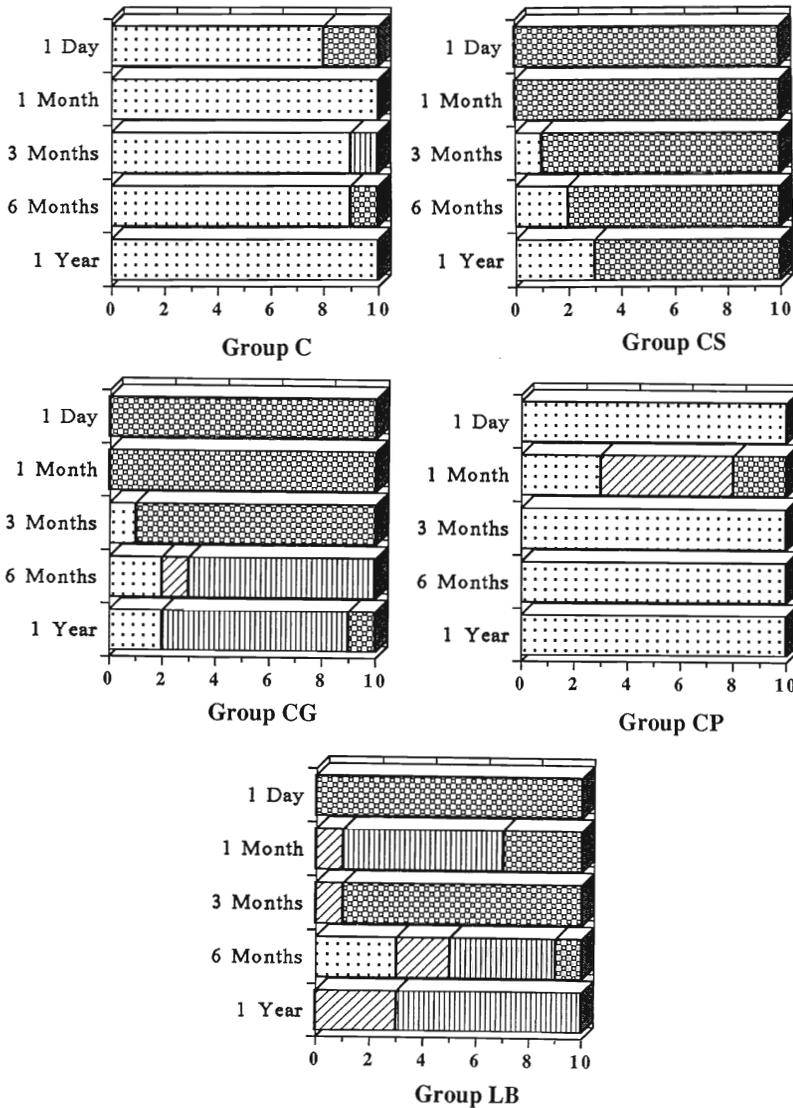
MICHAEL F. BURROW, *et al.*

Fig. 3 Fracture mode of groups conditioned with Ca agent.

months showed a majority of failures occurring cohesively in dentin. Adhesive failures were few, although an increase was noted from one day to three months. The greatest difference, however, was observed at the one-year period. At this test period, half of the specimens exhibited failure involving the resin component of the bonding system. At six months, three specimens showed partial adhesive failure between tooth and resin.

Group C: This group used the milder etching agent, Ca agent. The results showed a stable TBS up to one month, but a significant decrease in TBS at three months was recorded ($p < 0.05$) which remained stable from then on, being not significantly different up to one year. The pH of the solutions remained unaltered at pH 7.1 throughout all time periods. Mode
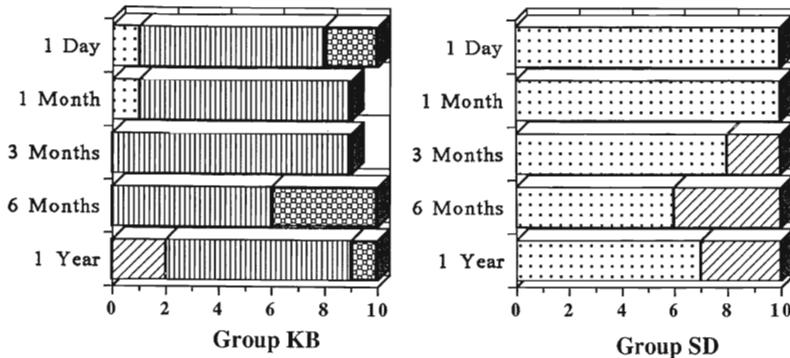
Fig. 4 Fracture mode of groups SD and KB.

Table 4. Change in pH of Groups

Group	1 day	1 month	3 months	6 months	12 months
K	*	7.6	7.1	7.1	*
KS	*	7.1	7.4	7.4	7.1
KG	*	7.6	7.0	7.1	7.4
KP	7.2	7.1	7.1	7.0	7.2
KSP	7.2	7.1	7.4	7.0	7.1
C	*	7.1	7.1	7.1	7.1
CS	7.2	7.1	7.1	7.1	7.0
CG	7.3	7.1	7.0	7.1	6.9
CP	7.4	7.1	7.1	7.1	6.9
LB	7.4	7.0	7.1	7.1	7.0
KB	7.3	7.1	7.0	7.1	7.0
SD	7.1	6.9	7.1	7.1	7.2

*: the pH figures for these times were not recorded.

of failure was principally adhesive in nature, although at one day, two specimens exhibited cohesive failure of dentin.

Group CS: The use of SA primer produced a large increase in the TBS as previously noted in Group KS. The one-day result was statistically higher than all other time periods (p<0.01). A large decrease in TBS was noted between one day and one month, and then it continued to further decrease up to the one-year result (p<0.05). However, from three months onwards the decrease in TBS were not statistically different. The pH of the solutions for this group was also very stable. Failure mode was mostly cohesive within the dentin, although at three months a

small increase of adhesive failure was noted.

Group CG: TBS of over 10 MPa were also obtained for this group at one day and one month, although from then on a slight decrease was seen by six months. At three months a statistically significant fall in TBS was found (p<0.01), but remained not significant beyond this period. Variation in pH of the solutions was small. Failure mode showed little change up to three months, consisting of almost all cohesive failures of dentin. At six months and one year, two adhesive failures occurred at each period. However of particular note was the very large increase of failures in the resin (Fig. 3). At six months and one

year, seven specimens each showed this type of failure.

Group CP: A statistically significant reduction in TBS was observed between the one-day and three-month results (p< 0.05). However, statistical variation was not determined between the one-day and one-month, one-month and three-month, three-month and six-month, six-month and one-year comparisons, indicating a small decrease in TBS; thus this group was relatively stable. Generally the TBS results were also lower like the other groups that did not use a primer. Fracture mode was always adhesive, except at the one-month period where five specimens exhibited partial adhesive failure and two specimens showed cohesive failure of dentin. This group showed the biggest variation in pH of the solutions ranging from pH 7.4 at one day to pH 6.9 at one year.

Group LB: The combination of SA primer and Protect Liner produced initially high TBS results at one day (13.4 MPa), but showed a steady decrease over the one-year period. Statistically significant variation occurred up to three months (p<0.05). From three months onwards the TBS was not significantly different and the six-month and one-year results were almost identical. Variation in fracture mode was very complex (Fig. 3). At one day and three months almost all the specimens showed cohesive failure of dentin. At one month the majority of failures were noted to have occurred in the resin (n=6). The six-month result exhibited three adhesive failures, four specimens exhibited failure only in resin, two partial adhesive and one dentin cohesive failure. By one year, seven specimens exhibited failure in resin, and the remainder produced partial adhesive failure. Changes in the pH of the solutions were negligible.

Group KB: This new experimental bonding system produced very high and very stable results over the 12 months. No time period showed any statistical variation with time and the lowest TBS recorded was 12.8 MPa. Variation in pH of the storage solutions was small. Failure mode was mainly within the resin (Fig. 4). Adhesive failures were recorded at one day and one month (n=1). Cohesive failure in the dentin was recorded at one day (n=2), six months (n=4), and one year (n=1). Two specimens at one year showed partial adhesive failure.

Group SD: Super Bond D-liner, the only chemically-cured material, produced the highest TBS of all groups. The TBS at one month (18.4 MPa) was very high, producing statistically significant differences with the three-month, six-month, and one year-results (p<0.05). However, a significant difference was not noted between the one-day and one-year results, indicating stability, although there was some reduction in the TBS over the one year. Fracture mode was generally adhesive in nature, although a slight increase in partial adhesive failure was observed after three months (Fig. 4). The pH of the solutions ranged from pH 6.9 at one month to pH 7.2 at one year.

DISCUSSION

In order to perform a long term investigation of adhesion to tooth substance, control of the storage solution for the specimens was believed to be very important from the aspect of pH stability and bacterial growth.

In a study by Muhlemann [13], it was shown that enamel hardness decreases with time when stored in physiological saline and to a slightly lesser degree in distilled water. Presumably this would also occur in dentin, though it has never been demonstrated. Also, from the aspect of the resin composite material, Chadwick *et al.*

[14] found that the compressive strength of resin composites increased over one year when stored in distilled water compared with two other solutions, lactate buffer (pH 4.0) and citrate buffer (pH 6.0). This was thought to be due to the storage medium conditions such as pH and ionic content.

Ion-exchanged water was selected because the active ions were removed, thus allowing a certain degree of control over the ionic content and reactivity of the water. The authors desired that when ion exchange occurred in the solution, that it be principally related to calcium (Ca). Additionally, it is known that saliva is also rich in Ca ions. Therefore, in the current study a Ca-rich storage solution was used. Plaster chips were added to the water so as to intentionally increase the concentration of Ca ions as a means to try to reduce Ca ion loss from the teeth. It was clear that the Ca content must have increased in the water, because the plaster chips were always eroded. For the one-year samples, the chips of plaster were reduced by 50–70% from the original size. Also the pH of the solution was noted to be always close to pH 7 when tested in a pilot study.

The study by Fotos et al. [12] indicated that when a method to control bacterial growth is not used, large changes in pH can occur in a short period of time. In the present study, bacterial growth was inhibited, but not completely, by the addition of 0.4% sodium azide to the solution used. It was observed that numerous teeth exhibited a small degree of bacterial growth by the presence of an orange-colored plaque-like layer that grew between the spacer and the resin composite on some specimens. The degree of bacterial growth was thought to be so minimal that it probably had little or no effect on the TBS and pH with regard to bacterial enzyme and metabolite production. A low of pH 6.9 up to a high of pH 7.6 was recorded, being always very close to neutral (pH 7) throughout the total test (Table 4).

The influence of the storage solution on bond strength from the aspect of hydrolysis is a very important problem for which almost no information is currently available. To date most studies have stored samples in water, distilled water, or saline, with no reference being made to the pH at the time of testing. Storage of teeth prior to test specimen production has been studied however, most often indicating that little or no effect on bond strength occurs despite the storage solution used, e.g., saline, distilled water, distilled water with thymol, etc. (Aquilino et al. [15], Finger [16], Rueggeberg [17]). Storage solutions which do not contain anti-bacterial agents such as thymol or sodium azide have no control over what type, or quantity, of hydrolytic and proteolytic enzymes may enter the storage solution. The study by Fotos et al. [12], using resins, found a quite large deviation in pH over a 60-day test period when non-sterilized, de-ionised water was used, but after sterilization, this deviation was almost completely eliminated.

It is of no doubt in the case of time-related studies, i.e., more than one week, the storage medium must be carefully controlled from the aspect of pH, bacterial growth, and ionic reactivity. Without such control, these influencing variables may affect the resin structure, as well as the dentin. Should this occur, comparison of the actual values of TBS over time is probably invalid. The current study was able to achieve control over pH stability.

Such influences as interfacial water diffusion between the bonding resin and tooth surface, swelling, and plasticization of the resin polymers as a function of time have yet to be fully investigated (Soderholm [7]).

Bovine teeth were chosen as the substrate due to size, considering greater simplicity of the experimental technique, as well as their availability. Similarly, it has been shown that TBS obtained by using bovine teeth are little or no different from those recorded using human teeth (Nakamichi *et al.* [18], Fowler *et al.* [19]).

The TBS variation amongst groups was noted to be quite large. In general, however, the TBS of those groups where a primer was not used were always much less than the groups in which a primer was used. On comparison of groups K and C, statistical variation was observed only at one month ($p < 0.05$) where the results of K-etchant were a little lower than expected, all other periods were not significantly different. The same effect was also observed when comparisons were made between groups KS and CS, KG and CG, KP and CP with no significant differences detected when compared at the same time period. However, the comparison of groups KSP and LB exhibited highly significant variations at six months and one year ($p < 0.01$). This difference in TBS could be explained by the fact that the mode of failure changed significantly. At the later time periods, failure in the resinous component greatly increased. Therefore, a direct comparison of groups KSP and LB is somewhat difficult and should be interpreted with some caution.

The effect of priming, either with Gluma or SA primer always produced significantly higher results for both conditioning agents. The one-day and one-year results between groups C and CS, or K and KS produced highly significant differences ($p < 0.001$).

The influence of Protect Liner on bond strength at the early periods was not always clearly detected. When only K-etchant was used with or without Protect Liner, no difference could be found. In the case of K-etchant conditioning, priming with SA primer and use or non-use of Protect Liner, no differences were detected at one day, one month and three months, but at six months a slightly significant difference could be found ($p < 0.05$), and by one year the difference was highly significant ($p < 0.001$) indicating the advantages of using Protect Liner. This may be explained by the increased curing time when Protect Liner is used in association with priming. Nikaido and Nakabayashi [20] and Nikaido [21] found that by increasing the curing time in light-cured systems, the TBS could also be significantly increased. When Ca agent was used, similar results were noted. At one year a better result was obtained when Protect Liner was used ($p < 0.01$) after only conditioning with Ca agent. However, when Ca agent and SA primer were used together with or without Protect Liner, the effect of the Protect Liner could not be detected. Why this was so is unclear. In this case, the effect of increased light-curing time was not apparent. When the fracture modes of CS and LB are compared, it can be seen that a large difference exists. This may be a contributing factor to the lack of observable differences in TBS.

Comparing groups LB and KB showed initially no variation in TBS, however, by three months large differences were detected ($p < 0.01$) which remained throughout the later test periods. The same observation was also noted when groups LB and SD were compared, although the results were only the same statistically at one day, from then on all comparisons were highly significantly different ($p < 0.001$).

On the other hand, both groups KB and SD produced high TBS over one year. However, the degree of variation was much greater in SD. The TBS results for KB in this study tend to be a little lower

than those of other studies (Fujitani *et al.* [22], Ogata *et al.* [23]). This was probably due to a variation in operator technique.

In general, all groups, with the exception of groups SD and KB, showed a decrease in TBS. These results correlate well with other studies, although different materials were tested. The results for Group K did differ from those determined by Tjan *et al.* [11]. Tjan *et al.* [11] concluded that the shear bond strength of K-etchant/Photobond was stable, whereas the current study found a significant decrease. This may be due to the fact that the bond test (Shear Bond Test *vs.* Tensile Bond Test), and also the storage media were different; Tjan *et al.* [11] used distilled water and did not indicate whether an anti-bacterial agent was added.

The reduction in bond strength is believed in the present study to not be necessarily related to the bond mechanism to tooth structure, but more to the resin structure itself and interfacial weaknesses that exist between the bonding resin and resin composite. Group LB provides a good example of this observation. Initially all specimens failed cohesively in the dentin. By one month, a large number of failures were detected involving partial adhesive failure, and failure within the resin. The failure within the resin was noted to involve not only cohesive failure, but also an adhesive component between the bonding resin and Protect Liner, and Protect Liner and resin composite. Although this trend was not detected at three months, by six months and one year most of the failures were observed to have occurred mainly in the resin, *i.e.*, involving very little tooth-resin type failure. These visual findings were confirmed by the SEM observations. Fig. 5 illustrates a typical example of this failure. The photograph in Fig. 6 shows the bonding resin separating from the dentin surface, and also the Protect Liner and bonding resin are also observed to be coming apart. Additionally, it can be noted that cohesive failure within the resin has occurred. Similarly, but to a lesser extent, Group KSP also showed this tendency.

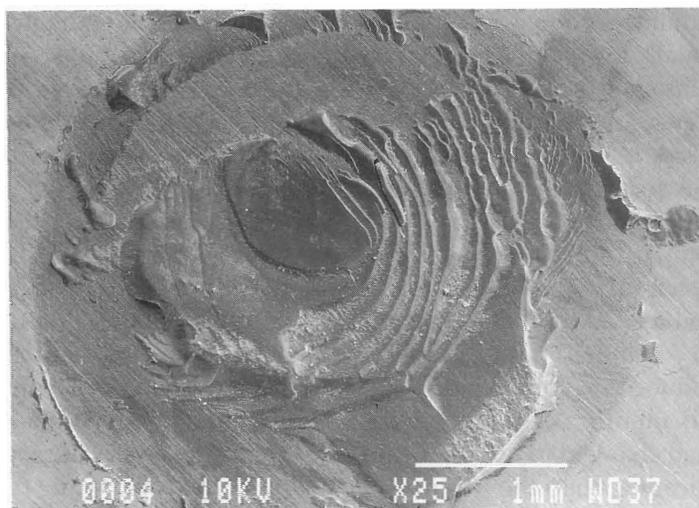Those groups where a primer was not used produced mostly adhesive failure

Fig. 5 SEM photograph of the fractured surface of a Group LB specimen at six-months showing the complex fracture mode exhibited in many specimens.

Fig. 6 SEM photograph of a six month specimen from Group LB. A combination of adhesive failure between resin and tooth, and adhesive/cohesive failure between the layers of bonding resin, Protect Liner, and resin composite can be detected.

between the bonding resin and tooth surface, despite which conditioning agent was used. Group CP, however, showed an unusual variation in the one-month result. At this time period, cohesive dentinal failure and partial adhesive failure were observed. Why such a variation occurred can not be explained. When a primer was employed, the failure mode was completely different, usually involving a large number of specimens showing cohesive failure in dentin. This was especially so when Gluma was used in association with K-etchant, and SA primer was used with Ca agent. An interesting point, though, is seen in the comparison of fracture mode variation between groups KG and CG. Group KG produced almost all specimens with cohesive dentinal failure, while Group CG produced no cohesive dentinal failures after six months. By that time, the failure mode had changed to failure within the resin, indicating that the resin had perhaps become a little weaker. This finding seems to be the reverse situation when SA primer was used. Group CS

initially produced an extremely high TBS, well above previous researchers' work (Sugizaki [4], Tagami *et al.* [24]). Group CS showed a slight increase in adhesive failures, whereas Group KS showed a marked increase of failures that were adhesive in nature. The TBS, however, were quite similar over the test periods, again indicating a likely weakening of the resin. These results might indicate that there is some degree of compatibility of conditioning materials and priming agents. It may be that different changes to the collagen occur when it is exposed to various conditioning agents.

Group SD is interesting in that it produced mostly adhesive failures throughout all test periods, although the TBS was always high. Kiyomura [8] demonstrated that the location of bond failure changed with time when Super Bond was tested. The same observation was also found in this study. Initially the failure tended to be between the surface of the tooth or hybrid layer and bonding resin. Later it was observed that this mode of failure still

existed to some degree, but also areas of the fracture site could be detected below the hybrid layer. It is believed the failure occurred at the base of the hybrid layer, as in Fig. 7. Kiyomura [8] also reported a large decrease in TBS over the first six months, 18 MPa to 8 MPa, and by five years the TBS had fallen to 3 MPa. This large decrease, however, was not found in the current study. This could, in part, be related to the pH control of the storage solution used in the current study. Additionally, a difference exists between Super Bond and Super Bond D-liner with the addition of HEMA as the priming agent. It therefore appears that HEMA improves the bond of this material, probably by enhancing the penetration of the bonding resin into the conditioned dentin. This has previously been demonstrated by Naka-bayashi [25]. An interesting observation for Group SD was that the number of failures in resin composite tended to in-crease with time. These failures involved cohesive failure within the resin compo-site. It seems that during the placement of

the resin composite, the as yet uncured bonding resin infiltrated the composite, thus making it more vulnerable to break-down at the later time periods.

Group KB produced perhaps the most remarkable fracture mode results, in that the majority of failures occurred between the bonding resin and resin composite. It was often observed that a layer of resin still covered the dentin surface and appeared shiny after the TBS test. This shiny appearance was similar to the appearance of the cured bonding resin. However, from the SEM observation, it appears that the mode of failure determined visually was not completely accurate. The SEM photograph (Fig. 8) indicates that the central portion tended to exhibit adhesive failure between the bonding resin and tooth surface, with the peripheral area consisting of the bonding resin. This mode of failure did not, however, vary greatly throughout the total test period. There-fore, the fracture mode seems to be related to a weakness of the bond between the bonding resin and resin composite. Such a
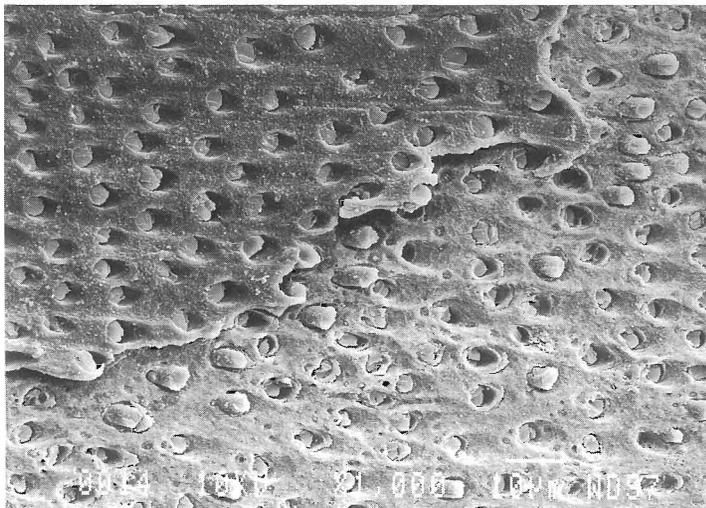

Fig. 7 One year specimen from Group SD. The SEM photograph depicts what is believed to be a region of failure at the base of the hybrid layer (right side). The left side of the photograph is thought to be the remnants of the hybrid layer. Tags of resin can also be very clearly seen.
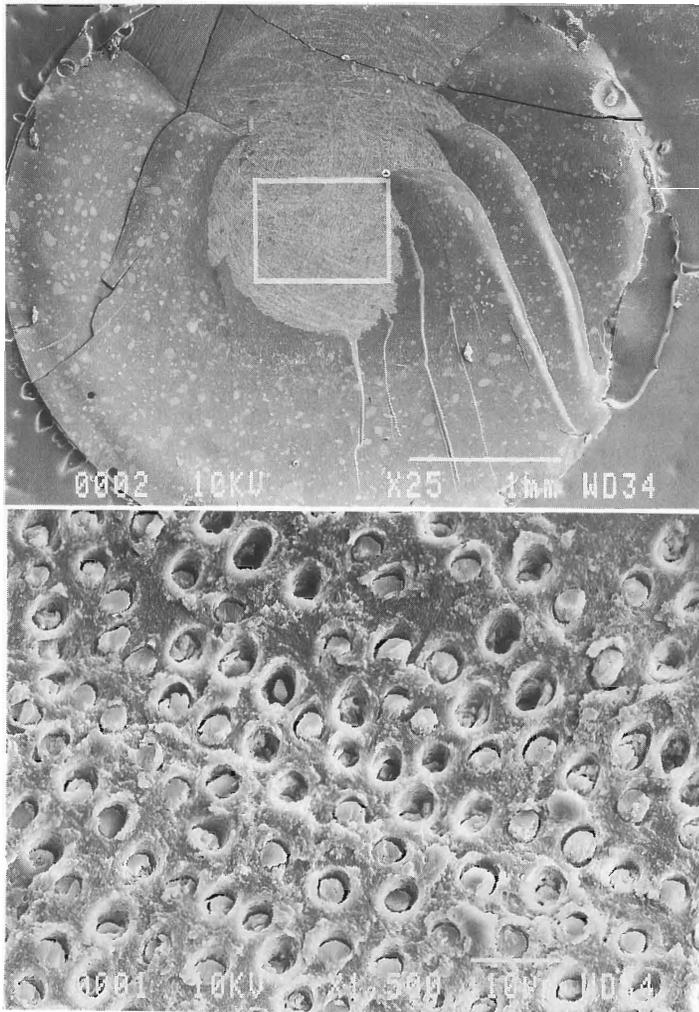
MICHAEL F. BURROW, *et al.*

Fig. 8 A 24 hour specimen from Group KB depicting the typical failure
mode exhibited throughout all time periods. The bonding resin
still covers most of the bonded surface. The central portion failed
adhesively. The lower SEM photograph is a high power view of the
area marked by the frame. Fractured resin tags can be seen in
many tubules, indicating that the smear layer had been removed
during conditioning.

location is believed to be somewhat weak
due to the fact that the curing of the
bonding resin may lead to a limited availa-
bility of free radical groups to bond to the
free radicals of the resin composite. This
might create a less than ideal chemical
union, making it possibly more susceptible
to hydrolytic degradation. Alternatively,

since this bonding resin contains filler
particles, it may act in a manner similar to
that seen when resin composite is added to
resin composite. Eliades and Caputo [26]
found that the oxygen-inhibited layer be-
tween adjacent resin composite layers
"substantially reduced interfacial strength."

A recent study by Watanabe and Naka-

bayashi [27] using a system which did not remove the smear layer by separate acidic conditioning, a similar idea to that of the KB system, showed very different results. They used an experimental light-curing bonding resin containing 5.0 wt% phenyl-P, 0.5 wt% camphorquinone, and 0.5 wt% N-phenylglycine in tri-ethyleneglycol dimethacrylate. The bonding resin was placed on the tooth surface, allowed to diffuse into the smear layer and superficial dentin prior to light-curing. The results at one day, six and 12 months were all much lower than Group KB. Their results also showed a significant decrease between the one-day and six-month, and one-day and 12-month results. Failure mode was observed to be complex in nature, involving failure of the resin as well as failure between the smear layer and tooth surface. Such failure between the smear layer and dentinal surface was not detected for the KB system. It is believed the conditioner of KB is acidic enough to dissolve the smear layer, and then slightly demineralize the dentin allowing a thin, but detectable, resin-impregnated layer (Hosoda et al. [5]). When conditioning solutions that simultaneously prime are used, it appears that a low pH (about pH 1.3) is essential to cause demineralization, so that the hydrophobic-hydrophillic components of the priming part can promote resin infusion into the dentin.

Ideally speaking, failure which leaves a layer of resin on the dentinal surface is probably advantageous in the clinical situation. Should failure occur, it is desirable that the dentinal surface still remain protected from invasion by bacteria and oral fluids. In the case of KB this may well occur. A further advantage of this system is the ease of use, involving simultaneous conditioning of enamel and dentin, and dissolution but intentional non-removal of the smear layer. It has often been stated

that opening of the dentinal tubules may allow ingress of toxic substances from bacteria, as well as egress of fluid to the cavity surface which can interfere with effective adherence by the bonding resin (Pashley [28]). All of the other systems exhibited qualities of failure that would most likely result in further damage to the tooth such as secondary caries, hypersensitivity and pulpal inflammation.

Those systems where mostly dentinal failure occurred could also be regarded as acceptable from the aspect of pulpal protection, since the bond strength between the tooth surface and resin was observed to be high. However, the trend of these systems by one year was for adhesive or partial adhesive failure to increase. It could thus be assumed that beyond this period of one year, the chance that more adhesive failures would occur is highly likely. Adhesive type failure should be considered as disadvantageous, since maintaining a vital pulp through the prevention of microleakage is unlikely in these systems.

Generally, the results of this study indicate that the use of conditioning agents in association with primers produce good bond strengths initially, but as time progresses the TBS tends to decrease significantly.

The current study aimed to investigate TBS durability, and from the results it is evident that no uniform pattern of change throughout all groups could be detected. If the current type of test is extended to five years, the variation in TBS that may occur can only be speculative. It is possible that the TBS may again decrease for those groups that initially stabilized, or the TBS may stabilize after two years as occurred in Kiyomura's study [8]. It seems, however, that from the results of this study, the evaluation of new bonding systems should include a durability test of at least six

months in length. The idea that initial high bond strengths at 24 hours can be maintained is a false premise in most cases. No doubt, a concurrent clinical trial is also necessary, since *in vivo* conditions are completely different from those of a static *in vitro* study. The use of thermal cycling to determine durability can not be regarded as being similar to long term storage like the present study. Such factors as water absorption into the resin, hydrolysis, as well as those factors related only to time can not be reproduced in short term tests of only a few days. Additionally, the thermal cycling test involves using temperature extremes up to 50°C or 60°C which are believed to alter collagen.

This study also evaluated failure of the bond. It is quite clear that fracture mode is not at all stable over time for most systems. In general, signs of change in the fracture mode only truly became evident by about six months. The reason for this may, in part, be related to the diffusion of water into the resin matrix which appears to take several months to reach saturation (Braden *et al.* [29]). Failure mode is one variable that has often been overlooked in many studies investigating tensile or shear bond strengths. This study clearly shows, however, that the way a material fails is very important, especially when related to time. A trend appears to be present which indicates that over time degradation in the resinous material increases. This implies that the bonding systems may still be functioning at the dentinal interface as designed, but the resin is beginning to fail. Clinically, this is clearly of importance, since the implication is that resin restorations may fail not only because of a poor bond to tooth structure but also due to inherent weaknesses in the restorative materials.

The results of the current work indicate the necessity that both long term TBS and

failure mode studies be performed. To obtain information that can be easily interpreted and compared, a carefully controlled storage solution should be used.

From this investigation it appears that certain features should be incorporated into the 'ideal' bonding system. Simplicity of technique is vital, as this should lead to less operator technique error. The bonding system should create minimal damage to the tooth surface during conditioning. Preferably the smear layer and very superficial dentin only should be disrupted or dissolved, and where possible the smear plugs should remain. By retaining the smear plugs, the permeability of the dentin should be lessened, thus helping to protect the pulp if microleakage occurs. It is apparent, from the current study, that those systems which formed a thin resin-impregnated layer resulted in the most stable adhesion. Ideally the material should also exhibit some degree of resilience in the bonding resin so as to counteract not only contraction of the curing restorative materials, but also flexure of the tooth during function.

Further areas of research that should be considered from the results of this work are: what effects water has on the degradation of the bond between the bonding resin and resin composite, since this could be a significant point of weakness as the TBS to dentin becomes stronger and more durable; what occurs to the bond and mode of failure when different storage solutions are used; what changes in dentin surface calcium content, and collagen occur during long term storage.

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