**In Vitro** Durability of One-bottle Resin Adhesives Bonded to Dentin

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Recently, one-bottle resins adhesives have been developed to reduce the number of clinical steps of resin application. They are now widely used in clinical dental practice. However, little is known regarding the detailed mechanism of bond degradation. Therefore, this study evaluated the durability of one-bottle resin adhesives using long-term water storage testing. Resin-dentin bonded specimens were prepared using five commercially available one-bottle resin adhesives. The specimens were sectioned perpendicular to the adhesive interface to produce beams and stored in distilled water for 24 hours (control), 100, 200, and 300 days. After the water storage, each beam was subjected to a microtensile bond test and then SEM fractography was performed on the fractured surface.

Compared to the bond strength at 24 hours after bonding (control), the bond strength of all tested adhesives were significantly decreased after 100 or more days in water. SEM fractography revealed a typical type of deterioration in the adhesive-composite interface that might cause a decline in bond strength after aging.

Keywords: One-bottle resin adhesive, Degradation, Hydrolysis

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**INTRODUCTION**

Recently, one-bottle self-etching systems have been developed with a view to simplifying the bonding procedure. Currently marketed dental adhesives can be divided into two categories: (1) etch-and-rinse adhesives that require pre-treatments with acidic etching and water rinsing; or (2) systems with a self-etching primer using an acidic monomer (Fig. 1). Furthermore, the self-etching systems can be classified as two-step and one-step types (with the latter available in all-in-one or one-bottle systems), according to the resin application time to the tooth surface (Fig. 1). With one-bottle adhesive, one drop of bonding resin from one container is applied to the tooth cavity, and the subsequent bonding step is performed by air-blasting and light-curing without acid etching or water rinsing. In this manner, the bonding steps of etching, priming and bonding are all done simultaneously.

Although resin application is simple and easy, previous in vitro studies have revealed several unfavorable disadvantages of all-in-one and one-bottle adhesives — namely, nanoleakage, water bubble formation, and phase separation at the adhesive interface. These shortcoming arise because of their increased concentrations of water and solvents (acetone or ethanol). Water is an essential component for demineralization of dentin hard tissue by the acidic monomer, while acetone and ethanol act as cosolvents with water for resin. However, the hydrophilic nature of bonding resins makes them vulnerable to water absorption, thereby leaching of the hydrophilic resin monomers and the adhesives behaving as a permeable membrane even after curing. As a result, hydrolytic degradation of the bonds occurs. At this juncture, it must be clarified that although short-term bonding defects (i.e. nanoleakage, water tree, and phase separation) have been shown in several reports, the basic reasons for bond degradation of one-bottle adhesive resin adhesives have not been clarified.

Therefore, the objective of this study was to evaluate the long-term durability of five one-bottle resin adhesives (self-etching systems) using a microtensile bond test and SEM fractography. The null hypothesis tested was that there is no difference in bond strength or failure distribution after 100,

![Fig. 1 Classification of adhesive resin systems.](image)

E: Etchant, P: Primer, B: Bonding resin
200, and 300 days of water storage.

MATERIALS AND METHODS

Tooth specimens
One hundred and twenty unrestored human third molars were collected after informed consent was obtained from patients under a protocol reviewed and approved by the institutional review board of Hokkaido University. The teeth were used within two months of extraction. Each tooth was sectioned perpendicular to its longitudinal axis using a diamond disk (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under a stream of water to expose a flat dentin surface (mid-coronal portion). Each surface was ground with 600-grit silicon carbide paper under running water for 30 seconds just prior to bonding.

One-bottle adhesives
Five commercially available one-bottle resin adhesives (Absolute/AB, AQ Bond Plus/AQP, G-BOND/GB, iBond/iB, and S² Bond/ S²) were used in this study (Table 1). Each bonding resin was applied on the dentin surface according to the manufacturer's instructions (Table 1). Following adhesive treatment, five 1-mm increments of a resin composite (AP-X, Kuraray Co. Ltd., Osaka, Japan) were built up and individually light-activated for 60 seconds. The resin-dentin bonded specimens were stored in distilled water at 37°C for 24 hours.

Microtensile bond test
The resin-dentin bonded specimens were cross-sectioned perpendicular to the adhesive interface by means of a diamond saw to produce beams (adhesive area: approximately 0.9 mm²) under water cooling/lubrication. Four beams were obtained per tooth. The beams were stored in distilled water at 37°C for 24 hours (control), 100, 200, and 300 days. The beams were then attached with a cyanoacrylate adhesive to a testing apparatus and a tensile load was applied with a material tester (EZ-test, Shimadzu Co. Ltd., Kyoto, Japan) at a crosshead speed of 1.0 mm/min until failure to obtain the ultimate tensile strength.

Table 1 Chemical formulations and bonding procedures of five one-bottle adhesives tested

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Chemical formulations</th>
<th>Resin application</th>
<th>Air-blast</th>
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<tbody>
<tr>
<td>Absolute (Dentsply Sankin, Tokyo, Japan)</td>
<td>methacrylate, phosphoric acid esters, acetone</td>
<td>Apply to tooth for 5 seconds with agitation</td>
<td>Gentle air-blast for 5 seconds</td>
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<tr>
<td>AQ Bond Plus (Sun Medical, Kyoto, Japan)</td>
<td>4-META, UDMA, monomethylacrylate, sodium, P-toluensulfinate, acetone, water</td>
<td>Apply to tooth for 5 seconds</td>
<td>Strong air-blast for 5 to 10 seconds after gentle air-blast for 5 seconds</td>
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<tr>
<td>G-Bond (GC, Kyoto, Japan)</td>
<td>methacrylate, phosphoric acid esters, 4-MET, UDMA, acetone, water</td>
<td>Apply to tooth for 10 seconds</td>
<td>Strong air-blast for 3 seconds</td>
</tr>
<tr>
<td>iBond (Heraeus Kulzer, Hanau, Germany)</td>
<td>4-META, UDMA, gutar dialdehyde, acetone, water</td>
<td>Apply to tooth 3 times during 30 seconds</td>
<td>Strong air-blast after gentle air-blast</td>
</tr>
<tr>
<td>S² Bond (Kuraray, Osaka, Japan)</td>
<td>MDP, Bis-GMA, HEMA, ethanol, water</td>
<td>Apply to tooth for 20 seconds</td>
<td>Strong air-blast for 5 seconds</td>
</tr>
</tbody>
</table>

Abbreviations:
Bis-GMA: bisphenol-glyceryl methacrylate
HEMA: 2-hydroxyethyl methacrylate
MDP: 10-methacryloyloxydecyl dihydrogen phosphate
4-MET: 4-acryloyloxyethyl trim ellitie acid
4-META: 4-methacryloyloxyethyl trim ellitate anhydride
UDMA: urethane dimethacrylate
strength. Bond strength values were calculated in MPa and were evaluated by two-way ANOVA and Fisher's PLSD test (p < 0.05; n=16-21 for each group). Bond strengths of beams that broke during specimen preparation were not recorded for the control (i.e. at 24 hours after bonding). Any beams that failed during the specimen fixation process were recorded as 0 MPa bond strength for the aged specimens at 100, 200 and 300 days.

**SEM examination**

After bond testing, the dentin side of the beam was immediately fixed in 2.5% glutaraldehyde in 0.1 M cacodylate buffer titrated to pH 7.2, for 72 hours. After which, the dentin side was rinsed several times with 0.1 M sodium cacodylate buffer. The beams were dehydrated in increasing concentrations of ethanol (40, 60, 70, 80, and 90%) for 30 minutes each and in 100% ethanol for 24 hours. Final chemical drying was conducted according to the protocol of Perdigão et al. using hexamethyldisilazane (Kyowa Chemicals, Tokyo, Japan). The dentin side of the fractured beam was sputter-coated with gold for 180 seconds and then analyze with a field emission scanning electron microscope (S-4000, HITACHI Ltd., Tokyo, Japan) at an acceleration voltage of 10 kV.

**Nanoleakage evaluation of silver nitrate**

Several resin-dentin bonded beams of each water storage period were randomly placed in 50 w/v% ammoniacal silver nitrate solution for 24 hours in the dark. Ammoniacal silver nitrate was prepared by dissolving 25 g of silver nitrate crystals (Sigma Chemical Co., St. Louis, MO, USA) in 25 mL of water. Concentrated (28%) ammonium hydroxide (Sigma) was used to titrate the black solution until it became clear as ammonium ions complexed the silver into diamine silver ions (\([\text{Ag(NH}_3]^+\)\). This solution was diluted to 50 mL with water, yielding a 50 wt% solution (pH=9.5). After silver staining, the specimens were rinsed thoroughly in distilled water and placed in photo-developing solution for eight hours under a fluorescent light. Subsequently, the microtensile bond test and SEM observation were performed as described previously. The bond strengths of silver stained specimens were not included in the bond strength results of this study. A schematic illustration of the current study's test design was shown in Fig. 2.

**RESULTS**

Figure 3 shows the mean bond strengths for five one-bottle adhesive systems as a function of the water storage period. For the control specimens, their bond strengths in descending order were: AQP, 43±12 MPa; S', 40±12 MPa; GB, 31±11 MPa; iB, 22±14 MPa; and AB, 14±5 MPa. After 100 days or more in water, the bond strengths of all groups were significantly decreased (p<0.05). For each resin

![Fig. 2 Test design.](image)
Fig. 4 Fractured surfaces of control specimens (a: iBond, b: G-BOND, c: S Bond, d: Absolute and e, f: AQ Bond Plus). Numerous air bubbles were present in the bonding resin layer (Fig. 4b, 4c, 4d). No void or crack formation was detected in the cohesive failure region of the resin composite, (Fig. 4e, 4f).
B: Bonding resin; C: Composite resin; H: Hybrid layer.
adhesives, there were no significant differences in bond strength among 100, 200, and 300 days (p>0.05).

Figure 4 shows the fractured surfaces of control specimens (24 hours after bonding). Numerous air bubbles of various sizes extended into the bonding resin layer for all control specimens (Figs. 4b, 4c, and 4d). However, no cohesive failure of the resin composite — in terms of void or crack formation — was detected (Figs. 4e and 4f).

Figure 5 shows the fractured surfaces of GB (Figs. 5a and 5b) and AQ (Figs. 5c and 5d) in the region of the hybrid layer after 100 days of water storage (Fig. 5b) and at the boundary between the bonding resin and resin composite (Figs. 5a, 5c, and 5d). Although the structure of the hybrid layer was intact (Fig. 5b), crack formation and detached filler particles were found in the adhesive-resin composite interface.

Figure 6 shows the fractured surface of an AB specimen that was stored in water for 200 days and placed in silver nitrate solution. The photos of Figs. 6a and 6b were taken from above, while Fig. 6c was obtained from a beveled direction. Large silver deposits were found in the rim of the specimen beam (Fig. 

Fig. 5  Fractured surfaces of G-BOND (Figs. 5a and 5b) and AQ Bond Plus (Figs. 5c and 5d) after 100 days of water storage in the region of the hybrid layer (Fig. 5b) and at the adhesive-composite interface (Figs. 5a, 5c and 5d). Although the micromorphological structure of the hybrid layer was almost completely intact (Fig. 5b), crack formation and detached filler particles were found in the adhesive-resin composite interface.

B: Bonding resin, H: Hybrid layer, F: Filler particle of resin composite; white arrows indicate filler particles of resin composite.
Fig. 6 Fractured surface of a specimen of Absolute. The specimen was stored in water for 200 days and then placed in silver nitrate solution for nanoleakage observation before the microtensile bond test. The photos of Figs. 6a and 6b are from above and that in Fig. 6c from the beveled direction for SEM observation. A schematic representation of the direction of SEM observation of the fractured surface is shown in Fig. 6d. The outer margin of the specimen beam was approximately 60 μm thick and was stained with silver nitrate (Fig. 6a). A water tree was observed at the border of the dentin and bonding resin (Figs. 6c).

Ag: Silver grains; B: Bonding resin; D: Dentin; W: Water tree; white arrows indicate the margin of the fractured surface of the specimen beam.

A water tree was also evident along the resin-dentin border (Figs. 6b and 6c).

Figure 7 shows the fractured surfaces of S' and iB in the region of the hybrid layer after 300 days of water storage (Figs. 7a, 7c, and 7d), as well as at the boundary between the bonding resin and resin composite (Figs. 7a and 7b). Crack formation between the filler particles and bonding resin matrix, and detached filler particles were found in the fracture region between the bonding resin and resin composite layer.

Figure 8 shows the fractured region in the internal resin composite (cohesive failure of resin composite) of an iB specimen immersed in water for 300 days. A schematic illustration of the fracture plane of this specimen is shown in Fig. 8b. No crack formation or detached filler particles were found in the resin composite.
Fig. 7  Fractured surfaces of S3 Bond (Fig. 7a), iBond (Fig. 7b) and G-BOND (Figs. 7c and 7d) after 300 days of water storage in the region of the hybrid layer (Fig. 7a, 7c and 7d), and at the adhesive-composite interface (Fig. 7b). Crack formation between the filler particles and bonding resin matrix, and detached filler particles are found at the fractured surface of the adhesive-composite interface.

B: Bonding resin, D: Dentinal tubule, H: Hybrid layer, F: Filler particle of resin composite.

Fig. 8  Cohesive failure region of the resin composite in an iBond specimen immersed in water for 300 days. A schematic illustration of the fracture plane of this specimen is shown in Fig. 8b. No crack formation or detached filler particles were evident in the fractured resin composite. F: Filler particle of resin composite.
DISCUSSION

Since etch-and-rinse systems utilize acid-conditioning pre-treatment, the disparity between the depth of demineralization and monomer diffusion due to defective resin infiltration creates a pathway for water invasion that accelerates the hydrolysis of bonds\(^{11,80}\). In particular, Tay et al.\(^{80}\) found increased nanoleakage within the hybrid layer or bonding resin in specimens aged for one year using an etch-and-rinse adhesive with comparatively hydrophilic resin. The main cause of bond degradation, when etch-and-rinse bonding is used, is the plasticizing effects of water on resin and collagen fibrils within the hybrid layer. However, in this study, resin-dentin bond degradation was characterized by breakdown in the adhesive-composite interface, apart from structural degradation of the hybrid layer in all the five tested one-bottle adhesive resins.

One-bottle adhesives are vulnerable to water sorption. As such, the adhesives behave like permeable membranes after bonding due to their high concentrations of water and solvents, coupled with a lack of hydrophobic resin coatings. The top surface of bonding resin is covered with uncured resin even after light irradiation, due to oxygen inhibition of the polymerization reaction. Hydrophilic bonding resin may be easily affected by air, leading to the creation of an unpolymerized layer on the bonding resin, and then the filler particles impregnated into resin by subsequent application of resin composite. This bond structure is typical of one-bottle adhesives, but not so for the other adhesives (i.e. two-step self-etching and three-step etch-and-rinse systems).

In the present study, neither gap formation nor reduction of filler particles was found in the adhesive-composite interface after 24 hours. However, after 100 days or more in water, the degradation pattern of filler reduction and gap formation was typical in this region for all the five adhesives — although they were not observed in the 24-hour specimens. Water penetrated into a water tree or nanoleakage occurred, resulting in the accumulation of water along the adhesive-composite interface. This contributed to bonding deterioration between the resin matrix and filler particles by hydrolysis over time. In addition, the bond strengths of controls specimens (i.e. 24 hours after bonding) were significantly (p<0.05) decreased after 100 days of water storage for all adhesives. Therefore, the null hypothesis must be rejected, since there were differences in bond strengths and failure distribution after 100, 200, and 300 days of water storage.

Recent studies have shown a credible relationship between the water sorption of resin and its hydrophilic nature\(^{80}\). For example, the water sorption behavior of bonding resins within the resin-dentin interface has been measured and evidenced by water fluid movement\(^{85}\) as well as by initial contraction polymerization shrinkage\(^{86}\). Further, the water sorption of bonding resins during and after bonding might increase as the amount of water or solvents increased, as shown by the one-bottle adhesives tested in the present study, leading to water transmission.

At 24 hours after bonding, the internal resin composite remained almost completely morphologically intact, as revealed by SEM (Fig. 4e and 4f). Moreover, although degradation was observed at the border between bonding resin and resin composite (Figs. 5a, 5c, 5d, and 7b), no structural change was found at the cohesive failure region of the resin composite at 1 mm from the resin-dentin interface in aged specimens (Fig. 8a). These results suggested that the closer the distance to the adhesive interface, the higher the bond degradation in the adhesives.

Typically, cohesive failure of resin composites or bonding resins are highly observed in specimens with high bond strength by SEM fractography\(^{80}\). However, in this study, many specimens showed low bond strength values with high percentages of cohesive failure of the bonding resin in the fractured surfaces (not shown). These observations indicated that the degradation of bonding resin highly contributed to reduction in bond strength.

Figure 6 shows a silver deposition emerging from the periphery of a specimen beam. It was approximately 60 μm thick and extended into the center of the resin layer at the fractured surface. It was thought that during 200 days of water storage, the resin material gradually disappeared from the periphery and infiltrated into the center portion of the beam. Nanoleakage was first found, by SEM examination, as silver nitrate staining within the adhesive interface by detecting deposition of infiltrated nano-sized silver particles\(^{80}\). In that study, the silver-stained interface was observed by the back-scatter mode of SEM instead of normal secondary mode. However, silver impregnation of the interface was clearly observed by the secondary mode of SEM in the present study.

Nanoleakage, manifested as silver grains or water tree with bubble-like silver deposits, was observed at the resin-dentin border or inside the bonding resin. To date, many studies have described water tree using TEM. However, no SEM report is available on water trees in resin-dentin bonds. This meant that in the present study, nanoleakage was severe enough such that its micromorphological pattern could be observed in the secondary image of SEM. Moreover, water trees normally extend from the upper part of the hybrid layer into the bonding resin layer in the resin-dentin adhesive interface. However, in the present study, the water tree that was found at the fractured surface extended from the
band of silver nitrate deposition around the margin of the specimen beam into the bonding resin layer. Thus, the direction of water tree extension was completely different from the previously described nanoleakage formation observed by TEM, despite a similar shape of the water tree. Based on these results, it seemed reasonable to suggest that water tree extension might indicate the direction of degradation within the resin-dentin bond. However, further studies using TEM are needed to clarify the effects of the morphology of water trees on the direction or pattern of bond degradation and structural changes of the hybrid layer.

In summary, this study clearly showed that bond strength was decreased due to the degradation of bonding resin. The nanoleakage at 24 hours after bonding and the subsequent resin extraction within the bonding resin layer in aged specimens might provide a site for water perfusion, resulting in accelerated bond degradation.

ACKNOWLEDGMENTS

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REFERENCES

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