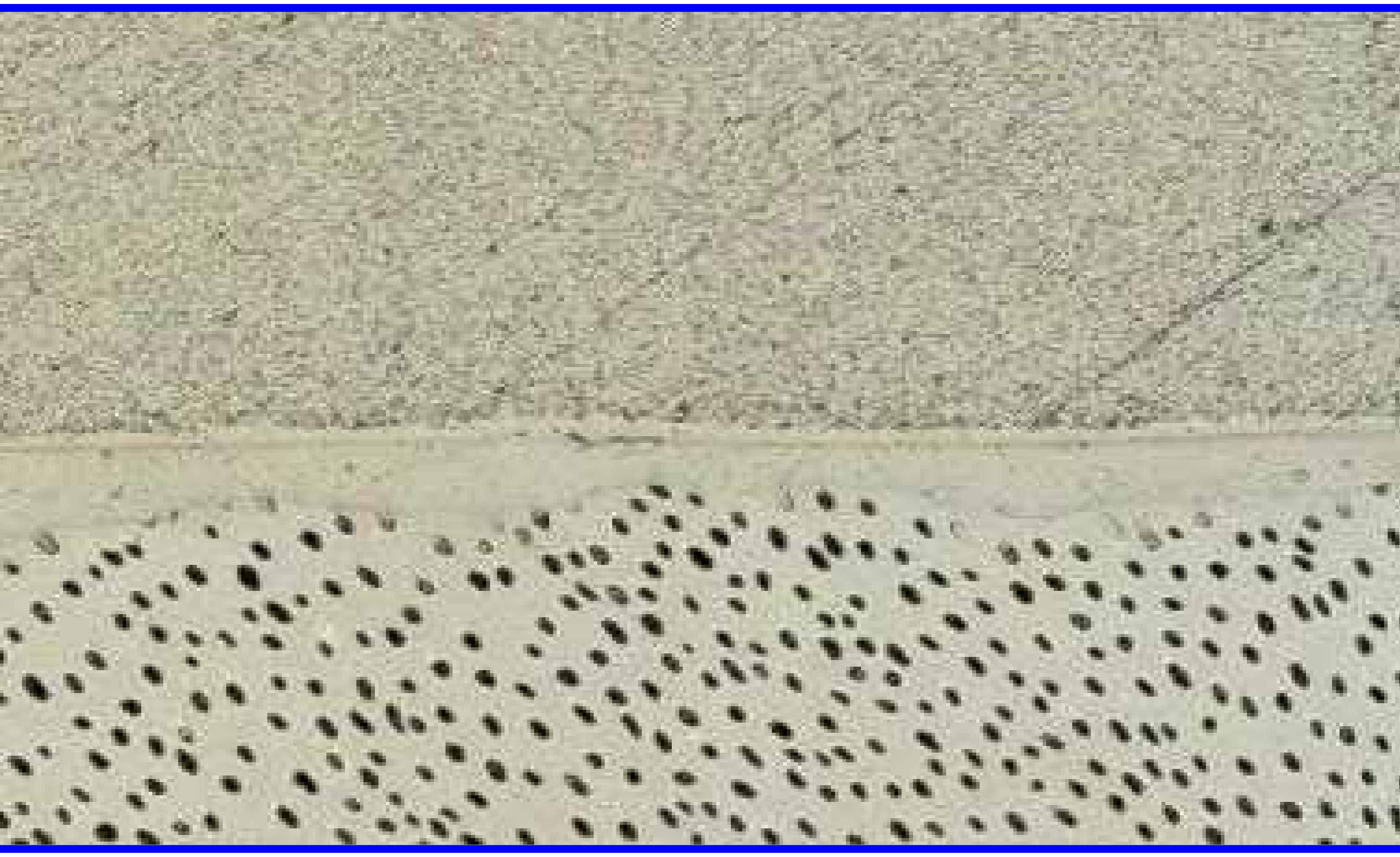
Tokuyama Dental

Technical Report



TOKUYAMA BOND FORCE

Single Component, Self-Etching, Light-Cured Dental Adhesive

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1. Introduction

Since the development of a method to make resin adhere to enamel by phosphoric acid etching in 1955,[1] dental bonding materials have advanced markedly. In particular, adhesion to dentin has improved markedly since the development of dentin primers in the 1980s. The GLUMA bonding system incorporating a dental primer consists of three steps: enamel etching using phosphoric acid; processing of smear-layer-covered dentin using EDTA; and improving the treated dentin and applying the bonding resin. Although this system improves adhesion, the primer increases the number of clinical steps. Dentists performing repair procedures while monitoring various conditions under clinical settings tend to regard the GLUMA bonding system as somewhat difficult to use.[2] The development of bonding materials since that time has focused on reducing the number of steps, with two-step systems becoming common. In Japan, self-etching systems incorporating a self-etching primer functioning as both etching and priming agents have been developed[3][4] (Shofu: Fluorobond, Tokuyama Dental: Mac-Bond II, Kuraray Medical: SEBond). In Europe and the U.S., total etching systems have been developed that contain a priming adhesive that functions as a primer and as a bonding agent following total etching using phosphoric acid (3M: Singlebond, Kerr: OptiBond Solo Plus, etc.). Total etching systems – also called wet bonding systems – are regarded as systems whose effectiveness is highly sensitive to technique, due to the difficulty of controlling moisture on the adhesion surface.[5]

In 1999, Tokuyama Dental introduced one of the world’s first one step system, called One-Up Bond F, which combined into a single self-etching step the three steps of etching, priming, and bonding. The One-Up Bond F bonding material is provided in two bottles, Liquid A and B, which must be mixed just before use. But recent years have also seen the introduction of various one-bottle/one-step bonding materials (Heraeus Kulzer: iBond, GC: G-Bond, Kuraray Medical: Tri S Bond, Dentsply: XenoIV, and Kerr: OptiBond All-In-One). These one-bottle/one-step bonding materials were developed with the primary goal of simplifying the bonding procedure, but are of lower dentin adhesion strength and adhesion durability than the above-mentioned two-step and three-step bonding materials.[5] Another disadvantage is that since most one-bottle/one-step bonding materials contain organic solvents, they are highly technique-sensitive at the blow-drying step.[6,7,8]

We undertook development to solve these problems, seeking to achieve both ease of use and high adhesion. In February 2007, Tokuyama Dental introduced Tokuyama Bond Force, a one-bottle/one-step bonding material containing an adhesive SR monomer with several functional groups per molecule that interact with dentin calcium. This one-bottle/one-step bonding material represents a revolutionary product that achieves levels of dentin adhesion comparable to two-step bonding materials through the following two actions: (1) stronger bonding to dentin at the molecular level due to the multiple-point interactions of the SR monomer; (2) higher adhesive layer strength due to three-dimensional crosslinking reactions between the SR monomer and calcium ion formed by demineralization.

2. Background

2-1 Total-etch system v.s. Self-etch system

Two major categories of bonding system currently available are total-etch and self-etch. These two categories occurred on the process that the field of developing competition of bonding system was shifting from conventional 3 step to new 2 step (figure 1).

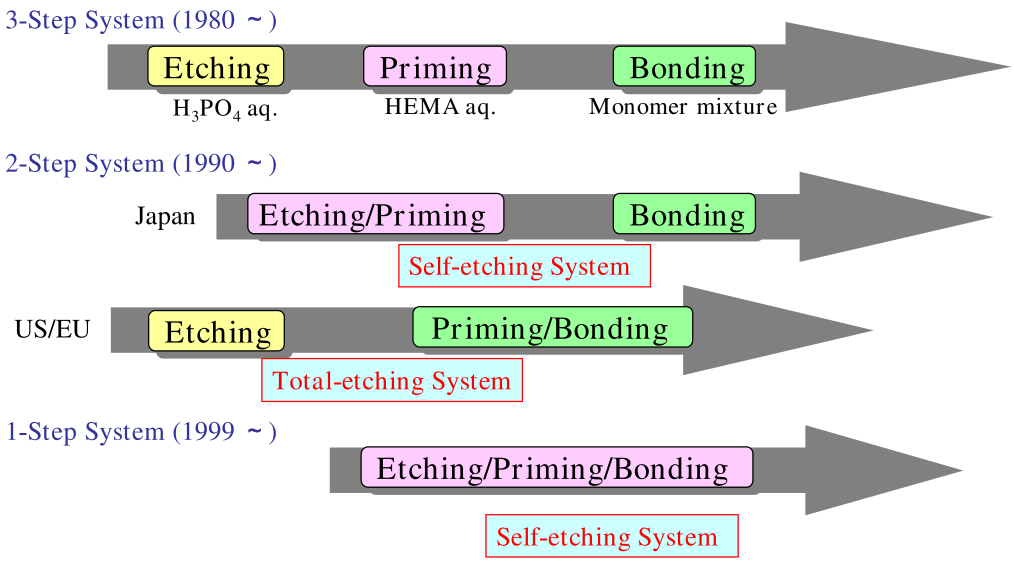


Figure 1 Developing history of Bonding systems

In total etch system, both enamel and dentin surface will be treated by phosphoric acid first to demineralize the enamel surface and to remove smear layer on the dentin. This treatment creates the etched surface where the bonding agent applied in the next step can penetrate and form mechanical retention with tooth structure. Composite resins can be chemically bonded to this bonding layer. However, recently it comes to be known that etching treatment and subsequent rinse and air drying step causes collagen collapse on the dentin surface, which inhibits penetration of resin monomer. As a result of this, a gap between bonding layer and dentin structure, in other words, the demineralized dentin without bonding penetration is formed. In order to verify the existence of the gap, we observed the interface between dentin and bonding layer of both total etch system and self etch system using micro-laser raman spectroscope (Figure 2). [15,16) ,17)] Figure 3 shows the result of raman analysis of the interface between total-etched dentin and bonding layer, which shows the existence of the gap where the intense of Hydroxyapatite is decreasing but intense of adhesive is hardly increasing. This gap may lead to lower durability of bond strength and cause post operative sensitivity.

In self-etch system, on the other hand, etching and penetration of bonding agent are processed at the same time, therefore, the gaps will not be occurred. This is one of major advantage of self-etch system. The raman analysis with self-etch system shown in Figure 4 supports this point. With self-etch system, strong adhesion and durability to dentin will be assured and risk of post operative sensitivity will be minimized.

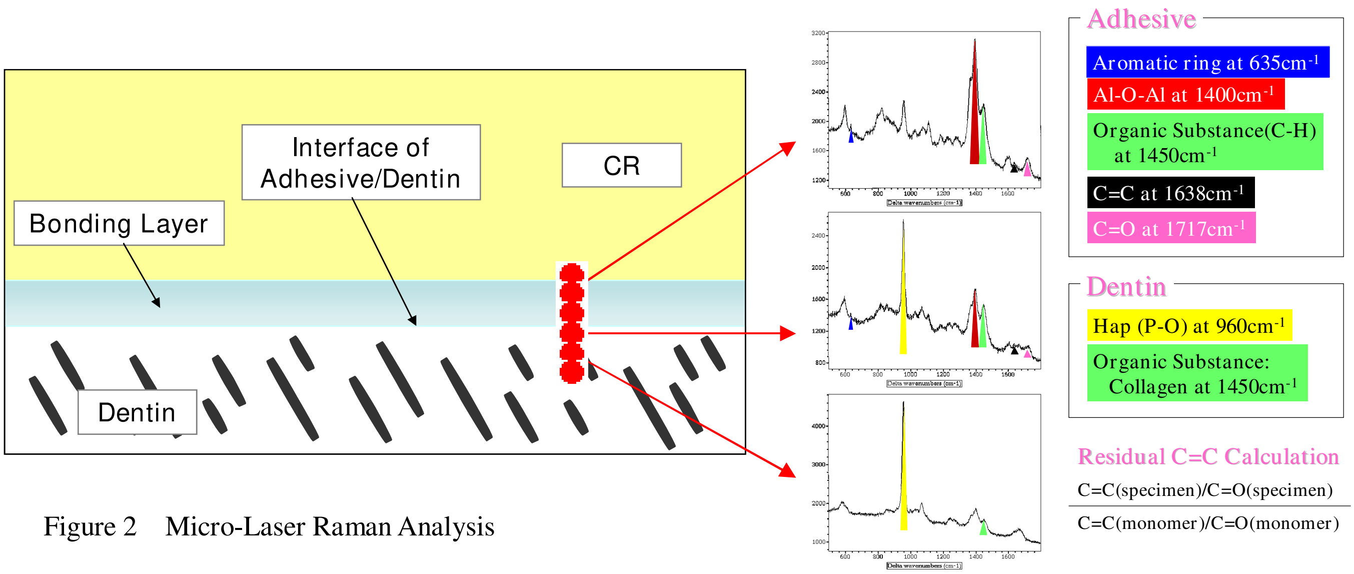


Figure 2 Micro-Laser Raman Analysis

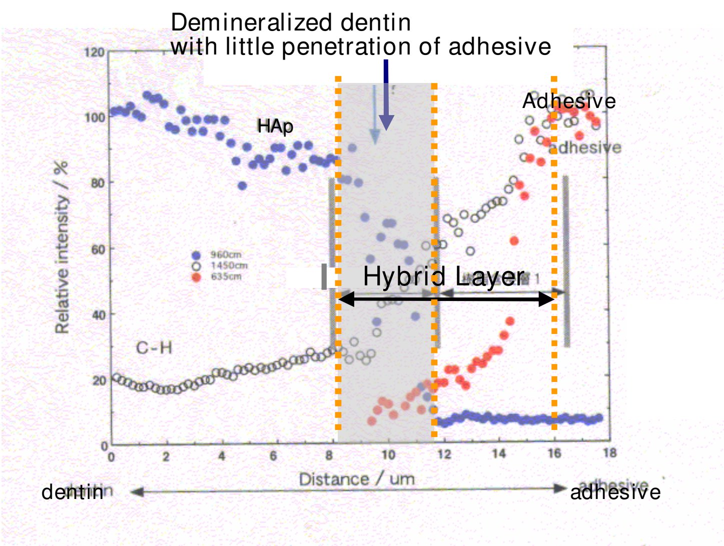


Figure 3 Interface of TE Bonding layer and dentin

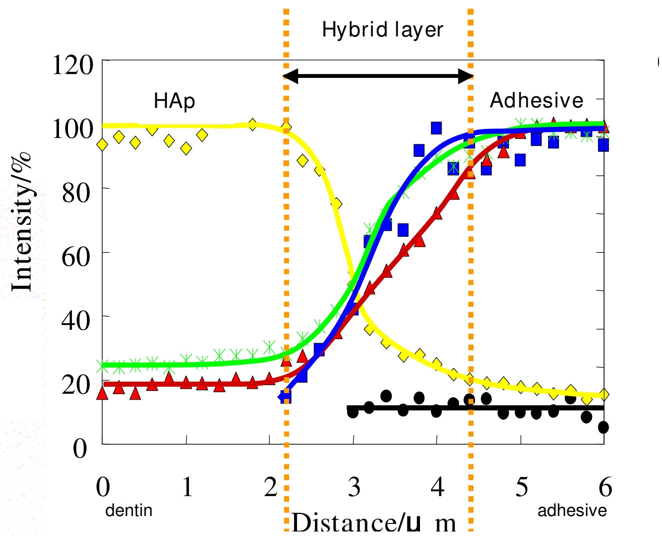


Figure 4 Interface of SE Bonding layer and dentin

2-2 Two-step bonding system v.s. One-step bonding system

Self-etching bonding system required to be equipped with components which function as etching agents, dissolving and eliminating smear layers. The components need to consist of two ingredients, an acid monomer and water at least. Since two-step bonding materials permit the addition of water to a primer, the bonding material that eventually becomes the bonding layer does not contain water. Table 1 gives the composition of conventional two-step and one-bottle/one-step self-etching bonding materials. All the one-bottle self-etching bonding systems contain a soluble organic solvent such as acetone, water, and an acid monomer in one bottle all together. It is assumed that this is the most significant difference from two-step systems, which contributes to the low adhesion strength, low adhesion durability, and high technique sensitivity of one-step bonding system.

Figure 5 compares the adhesion performance of conventional two-step and one-bottle/one-step self-etching bonding systems. The figure shows significantly lower bond strength and durability for one-bottle/one-step systems compared to two-step systems. With G-Bond and iBond, when acetone is evaporated by air-drying, the water in the bonding material may cause phase separation, lowering bond strength and durability. Because Tri S Bond contains hydroxyethyl methacrylate (HEMA), a relatively hydrophilic substance, the evaporation of ethanol (the solvent) does not cause phase separation. But adding hydrophilic HEMA reduces water resistance, thereby reducing bond strength and durability.

Table 1 Composition of several bonding materials

Bonding Agent	Type	Composition	
SE BOND(SE) Kuraray	2 Step	Primer	Acid monomer HEMA Water Photopolymerization catalyst
		Bond	Acid monomer HEMA Bis-GMA Silica filler Photopolymerization catalyst
Tri S Bond(TS) Kuraray	1 Bottle 1 Step	Bond	Acid monomer HEMA Bis-GMA Water Ethanol Silica filler Photopolymerization catalyst

G-Bond(GB) GC	1 Bottle 1 Step	Bond	Acid monomer Multifunctional monomer Water Acetone Silica filler Photopolymerization catalyst
Xeno IV(Xeno) Dentsply	1 Bottle 1 Step	Bond	Acid monomer Multifunctional monomer Polymerization catalyst Cetyl Amine Hydrofluoride Water Acetone
iBond(iB) Heraeus Kulzer	1 Bottle 1 Step	Bond	Glutaral aldehyde Acid monomer Other monomer Photopolymerization initiator Water Acetone

*HEMA: hydroxyethyl methacrylate, Bis-GMA: Bisphenol A di(2-hydroxypropoxy)di-metacrylate, 3G: triethylene glycol

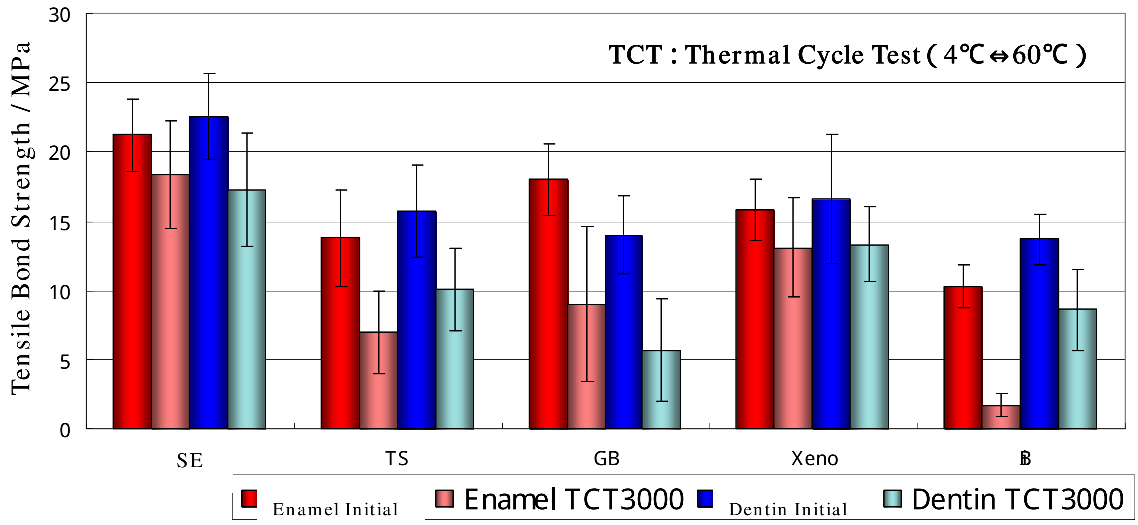


Figure 5 Tensile bond strength of several bonding systems (tested on bovine teeth)

As mentioned above, developing a one-bottle/one-step bonding material with sufficient adhesion performance requires forming a highly water resistant adhesion layer under severe conditions – in short, high water content. This layer must bind strongly to dentin. To form such a layer, Tokuyama Bond Force (introduced in February 2007) employs a 3D-SR (self-reinforcing) technology.[9,10] With 3D-SR technology, the adhesive SR monomer in the bonding material achieves: 1) multiple-point interactions with dentin; 2) three-dimensional crosslinking reactions with calcium ions; and 3) three-dimensional crosslinking polymerization. Ultimately, these processes form an insoluble adhesion layer that reacts strongly to the dentin calcium ions on the adhesion interface. This technology resolves the above-mentioned problems associated with one-bottle/one-step bonding materials. Chapter 4 discusses the Bond Force adhesion mechanism.

3. Features of Tokuyama Bond Force

3-1 Ease of use

Tokuyama Bond Force is a one-bottle/one-step bonding material that requires no preprocessing. Figure 6 explains how it is used.

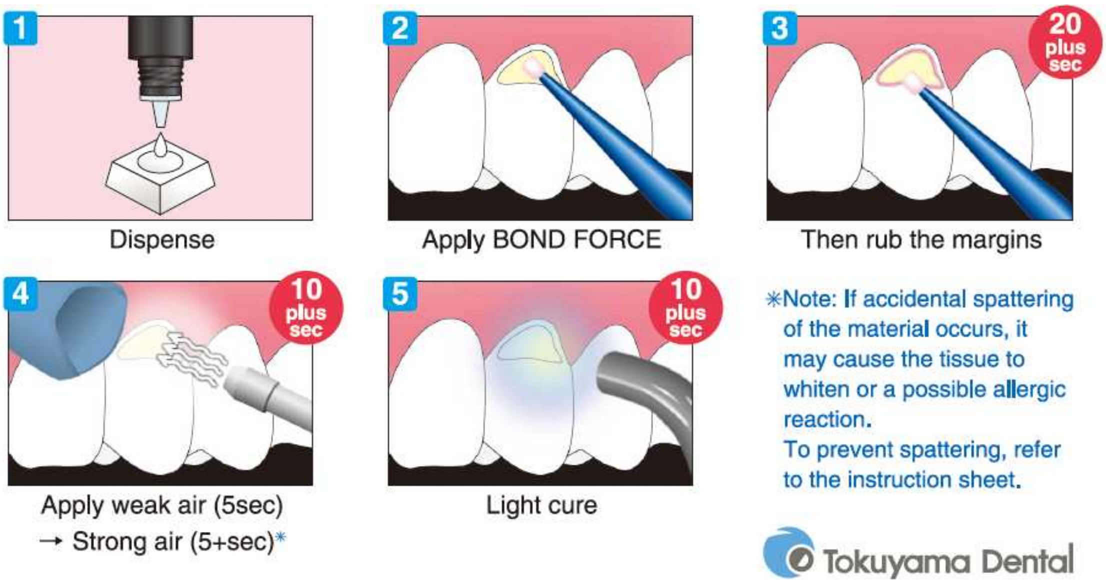


Figure 6　Procedure of Bond Force

After being applied to a cavity, the bonding solution is allowed to stand for 20 seconds. The area is then air-dried for ten seconds and irradiated with light for ten seconds. These procedures are both simple and convenient.

3-2 Superior adhesion performance

Although Tokuyama Bond Force is a one-bottle/one-step bonding material, it is a revolutionary bonding material that adheres readily to dentin. We used the adhesion test methods shown below to assess the initial adhesion performance and durability (4/60˚C thermal cycle) of Bond Force. Figure 7 provides the results.

Adhesion test methods

(1) Emery paper (#600) was used to polish bovine teeth, and a piece of tape with a 3-mm hole was applied to the enamel or dentin surface of each tooth. The present product was then applied to the hole.

(2) The teeth were allowed to stand for 20 seconds and blow-dried to evaporate the solvent.

(3) A dental polymerization light-curing unit was used to apply visible light for ten seconds.

(4) A board wax with an 8-mm hole was attached, and the hole was filled with a composite resin paste, followed by visible light irradiation for 30 seconds.

(5) The board wax was removed. After soaking the tooth in 37˚C water for 24 hours, we attached the tooth to an 8-mm stainless steel tension-measuring jig using an instant adhesive, then measured the tensile adhesive strength four times with each bonding material using a constant-speed stretching test machine (tensile speed: 2 mm/min) to obtain the average tensile adhesive strength.

* Bonding materials tested

Bond Force (Tokuyama Dental), Tri S Bond (Kuraray Medical), G-BOND (GC), XenoIV (Dentsply), iBond (Heraeus Kulzer), OptiBond All-In-One (Kerr), Easy Bond (3MESPE), SE Bond (Kuraray Medical), Single Bond Plus (3MESPE)

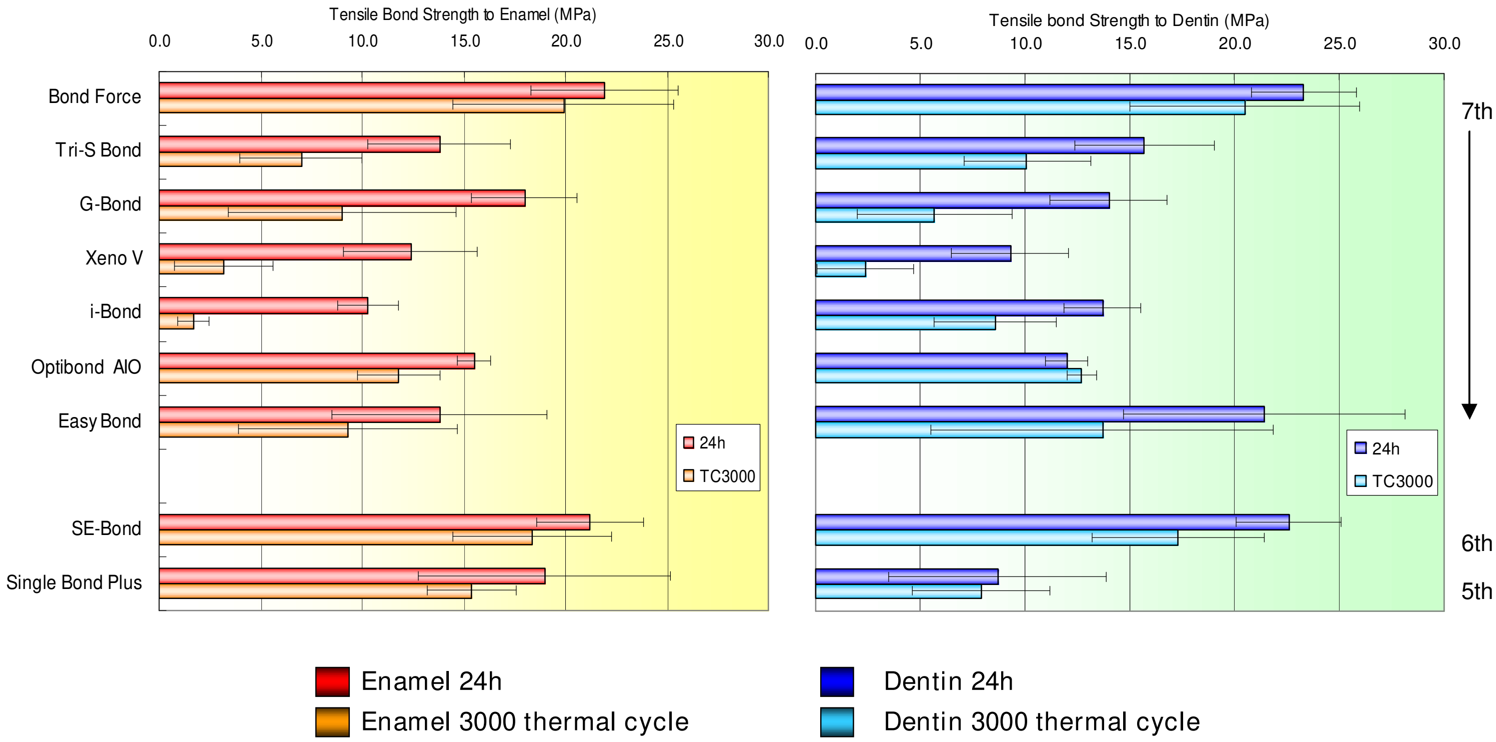


Figure 7 Tensile bond strength

The Bond Force initial bond strength to dentin and to enamel are significantly higher than for other one-bottle/one-step bonding materials (7th) and are comparable or superior to two-component bonding materials (5th and 6th) (Figure 8). Bond strength after 3,000 thermal cycles for other one-bottle/one-step bonding materials dropped markedly from the initial strength, while the bond strength of Bond Force remained constant after 3,000 thermal cycles. After 10,000 thermal cycles, the bond strength of Tokuyama Bond Force to enamel and to dentin was 21.0±3.4 and 19.7±2.7 MPa, respectively. Tokuyama Bond Force showed an adhesion durability comparable or superior to SE Bond, a two-step bonding material.

The specific results given above were obtained through a study by Tokuyama Dental, as Table 2 shows, but the superior adhesion performance of Bond Force has been demonstrated in many university studies.

Table 2. University studies

University	Method	Result	Dentistry
Hokkaido university	Micro Tensile (Human teeth)	Bond Force：70.9±16.0 MPa SE BOND ：59.9±23.4 MPa	2006 Autumn Conservative Dentistry(JP)
Tokyo Medical and Dental University	Micro Tensile (Human teeth)	Bond Force ：45.7±4.7 MPa SE BOND ：48.0±7.8MPa Tri S Bond ：40.7±6.8 MPa G-Bond ：39.4±9.1 MPa	2006 Autumn Conservative Dentistry(JP)
Okayama University	Micro Tensile (Human teeth)	Bond Force： 62.8±14.3(n=10)MPa OBF-Plus ： 49.3±16.6(n=10)MPa Tri S Bond： 49.7±3.5(n=10)MPa Absolute ： 24.8±6.6(n=10)MPa SE BOND ： 66.4±3.3(n=10)MPa	2007 Spring Adhesive Dentistry(JP)
Toranomon Hospital	Micro Tensile (Human teeth)	Bond Force ：50.0±9.8 MPa SE BOND ：49.4±10.0 MPa	2007 IADR 2007 Spring Adhesive Dentistry(JP)
Aichi Gakuin University	Micro Tensile (Human teeth)	Bond Force ：36.3 MPa Single Bond：33.5 MPa	2007 IFED 2007 Spring Conservative Dentistry(JP)
University of North Carolina	Micro Tensile (Human teeth) after 2 year	Bond Force ：38.8±13.9 MPa SE BOND ：31.3±12.8MPa Optibond All-In-One ：32.2±11.7 MPa Xeno IV ：28.3±11.9 MPa iBond ：17.0±8.6 MPa Adper Prompt ：15.3±9.7 MPa	2010 AADR

※ IFED: International Federation of Esthetic Dentistry
IADR: International Association for Dental Research
AADR: American Association for Dental Research

3-3 Effects of air-drying on adhesion strength

Most one-bottle/one-step bonding materials contain volatile organic solvents, not simply to improve the penetration of an adhesive into dentin, but to promote azeotropic removal of water added to demineralize dentin when volatile organic solvents are evaporated by blow-drying after applying a bonding solution. Existing one-bottle/one-step bonding materials are technique-sensitive, with the extent of blow-drying used to evaporate the solvent affecting adhesion strength. In contrast, the adhesion strength of Tokuyama Bond Force is designed to be independent of blow-drying (bonding thickness). This advantage is attributable to SR technology, discussed further below.

To assess the effects of blow-drying on adhesive strength, we performed a microtensile adhesion test by the following methods. Table 3 and Figures 8 show the results.

Microtensile test methods:

(1) A human tooth (molars, occlusal surface) was polished using P120 followed by P600 waterproof abrasive paper parallel to the labial surface to expose the dentin surface.

(2) The entire dentin surface was treated with a bonding material (with the extent of blow-drying following application varied to create the samples).

(3) On top of the bonding surface, a composite resin (Palfique Estelite A3) was applied to a layer height of at least 4 mm. The tooth was soaked in 37°C water for 24 hours.

(4) An instant adhesive [Model Repair II (Sankin)] was used to attach the tooth to a quick-cured block. The block was attached to a diamond cutter to slice the tooth to a thickness of 0.7 mm. For the slices obtained in (3), thickness (A) was measured using a micrometer.

(5) The interface of each slice with which thickness (A) was measured was trimmed to the shape of an hourglass with a dental turbine. At this point, great care was taken so that the tip of both trimming curves would be on the interface surface. We determined the interface width of each slice (B) by the following formula:

Width (B) = adhesion area 1 mm^2/slice thickness (A)

(6) The interface width of each slice (B) was measured using a micrometer.

(7) Before tensile testing, the bonding thickness of each test slice was measured using a microscope. A trimmed sample was fixed to the jig using an instant adhesive. At this point, the adhesion interface surface of each sample was set at the middle of and parallel to the jig. (2) The jig was set to an autograph (Shimadzu). A tensile test was performed under the following conditions.

Crosshead speed: 1 mm/min, load unit: 1 N, Area: 1.0 mm^2, Full load: 500N

Table 3. Film Thickness and Bond Strength (to human dentin)

Product	Type	Air-Drying (pressure)	Film Thickness/µm	Bond Strength /MPa
Bond Force BF	1 bottle, 1 Step	Strong	3.7±0.8	59.5±8.0
		Medium	10.3±2.0	60.4±3.9
		Weak	29.0±4.5	53.8±6.6
SE BOND SE	2 Step	Strong	8.0±1.0	19.2±5.6
		Medium	12.3±1.4	30.5±4.1
		Weak	97.7±9.4	56.4±13.9
Tri S Bond TS	1 bottle, 1 Step	Strong	8.0±0.8	37.3±13.4
		Medium	11.3±1.4	34.6±4.5
		Weak	30.2±7.6	28.7±9.2
XenoIV Xeno	1 bottle, 1 Step	Strong	3.6±0.9	25.4±5.1
		Medium	12.8±3.9	53.1±14.4
		Weak	17.3±2.3	29.6±11.6
i-Bond iB	1 bottle, 1 Step	Strong	9.2±1.3	18.2±6.7
		Medium	23.5±3.8	20.2±8.1
		Weak	32.4±7.0	12.9±3.3
OptiBond All-In-One OP	1 bottle, 1 Step	Strong	5.8±1.1	42.4±5.3
		Medium	13.3±4.4	40.5±4.7
		Weak	17.5±4.8	15.9±5.0

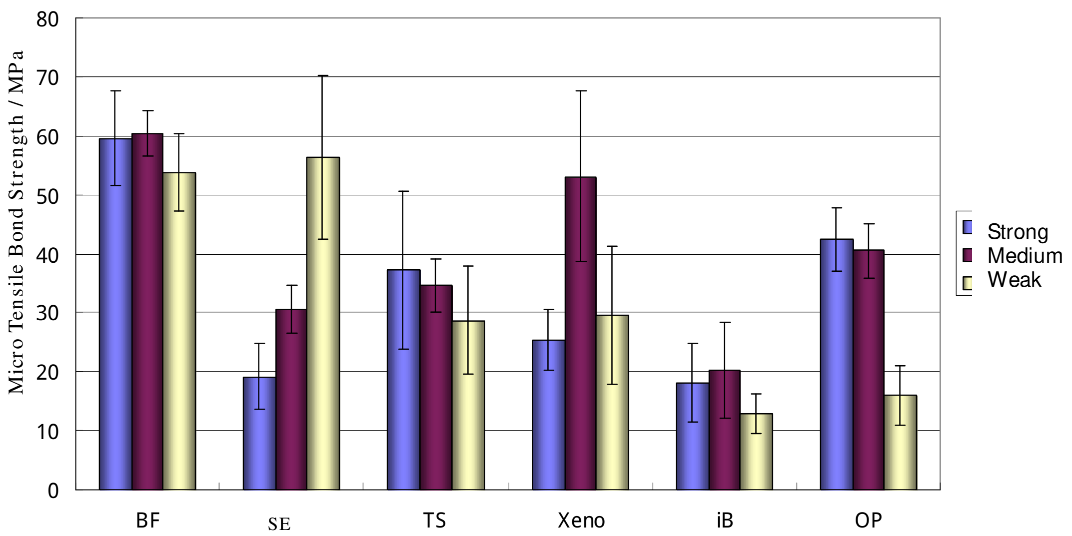


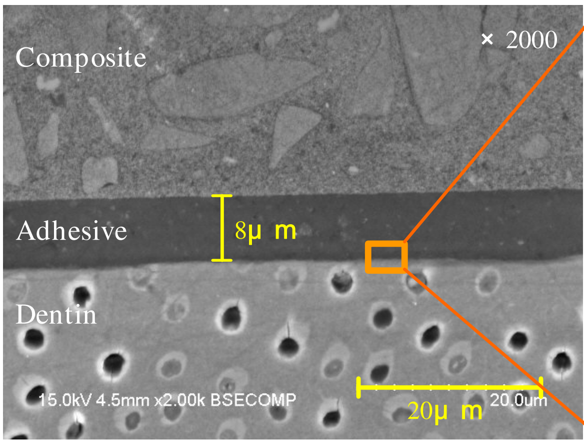
Figure 8 Influence of air-drying on bond strength(human dentin)

With Bond Force, a high bond strength of ≥50 MPa was maintained at bonding thicknesses from 3 to 30 μm, clearly demonstrating its relative immunity to differences in air-drying. Applying Tokuyama Bond Force to a thickness of ≥30 μm was quite difficult, due to the low viscosity of the bonding material and the presence of a solvent. With OP, iB, and Xeno, air-drying at low pressure tends to reduce bond strength; with SE and OBFP, air-drying at high pressure tends to reduce bond strength. TS was insensitive to the extent of air-drying but offered lower bond strength than the other systems.

Since high bonding thickness creates cosmetic issues (cleavage lines) post-therapy, thinner bonding materials are in greater demand. This makes Bond Force a highly useful clinical bonding system.

3-4 Observation of the adhesion interface

Figures 9 and 10 are SEM images of the Bond Force adhesion interface (human tooth dentin/bonding interface). After Bond Force application, we performed air-drying at low pressure for 5 seconds and at medium pressure for 5 seconds, forming a very thin bonding layer of 8 μm (Figure 10). Figure 11, an enlarged view of the dentin/bonding layer interface, shows an excellent interface free of gaps.



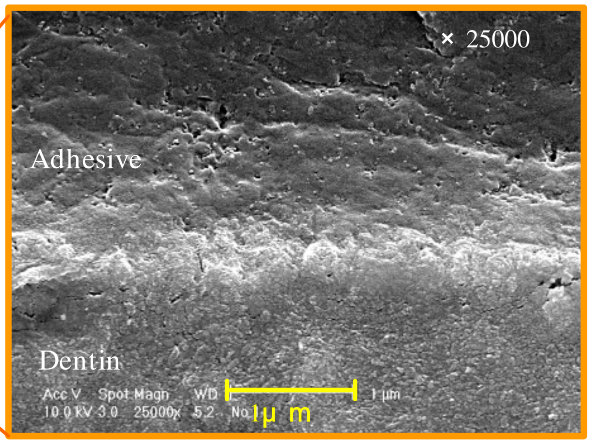


Figure 9 SEM image of adhesion interface

Figure 10 Enlarged View of figure 10

Figure 11 shows an SEM image of the Tokuyama Bond Force adhesion interface (following argon etching). We see a good interface free of gaps and obvious resin-impregnated layers. However, TEM image of the same interface showed a very thin resin-impregnated layer of 0.2-0.5 μm at the interface (Figure 12). (Figures 11 and 12 and their assessment were provided by Professor Tagami at Tokyo Medical and Dental University.)

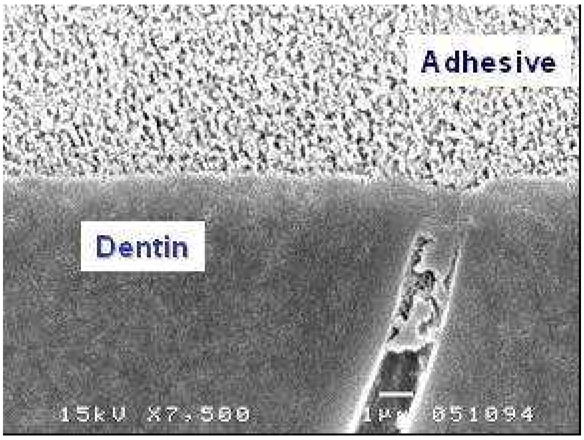


Figure 11 SEM image of adhesion interface (provided by Professor Tagami)

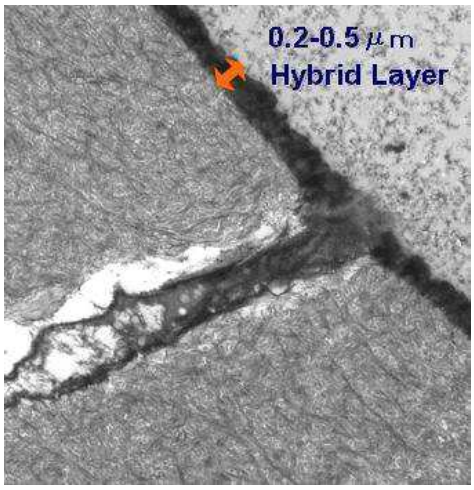


Figure 12 TEM image of adhesion interface (provided by Professor Tagami)

According to recent study on adhesive performance of bonding systems in Tokyo Medical & Dental University, it is verified that functional monomer contained in the self-etching bonding system chemically bond to hydroxyl apatite of tooth structure, forming "acid-base resistant zone (ABRZ)" called "Super Dentin" or "Super Enamel" which reinforced tooth against demineralization resulting from an acid attack [14]. Super Dentin or Super Enamel is created right under the hybrid layer in self-etching bonding system at the adhesive/resin interface and observed with Tokuyama Bond Force (Figure 13) as well. Since the ABRZ is not found when total-etch bonding system was used, forming ABRZ is one of big advantage of using self-etching bonding system, which will lead to improve long term results and durability of composite resin restorations.

<u>Test method</u>

1. Prepare the extracted human dentin treated with Tokuyama Bond Force and place a composite resin on it
2. Cut the specimen vertically to the bonding interface
3. Immerse the specimen into acidic solution and then basic solution
4. Examine the bonded interface by SEM

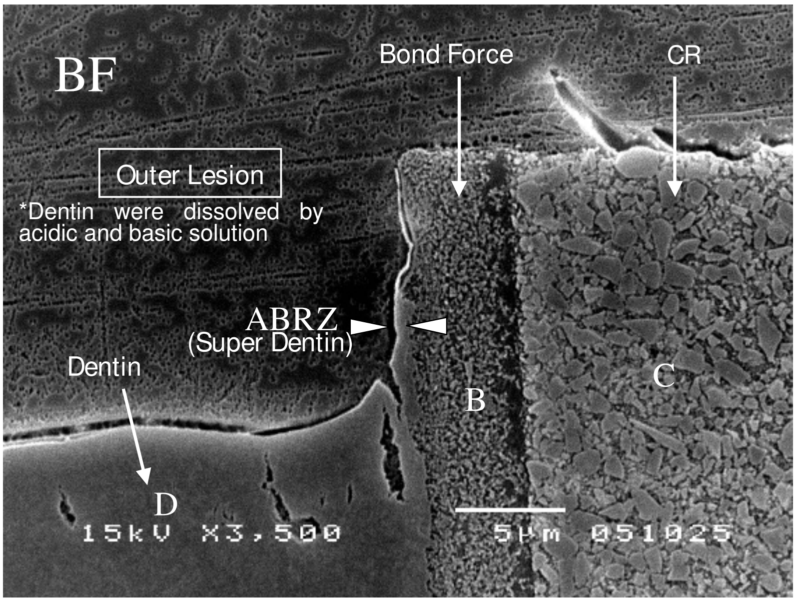


Figure 13 Super Dentin created by Bond Force
(provided by Professor Tagami)

3-5 Cavity adaptation

Figure 15 to 21 are laser microscope images showing cavity adaptation of several boding system using the specimens prepared as shown in Figure 14.

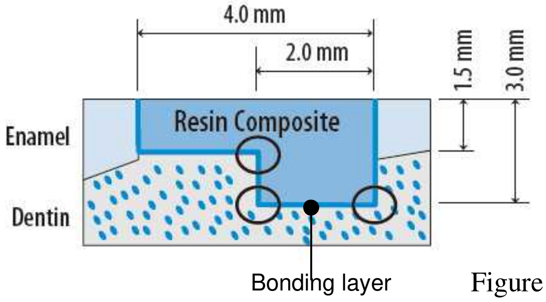


Figure 14 Cavity model for microscope observation

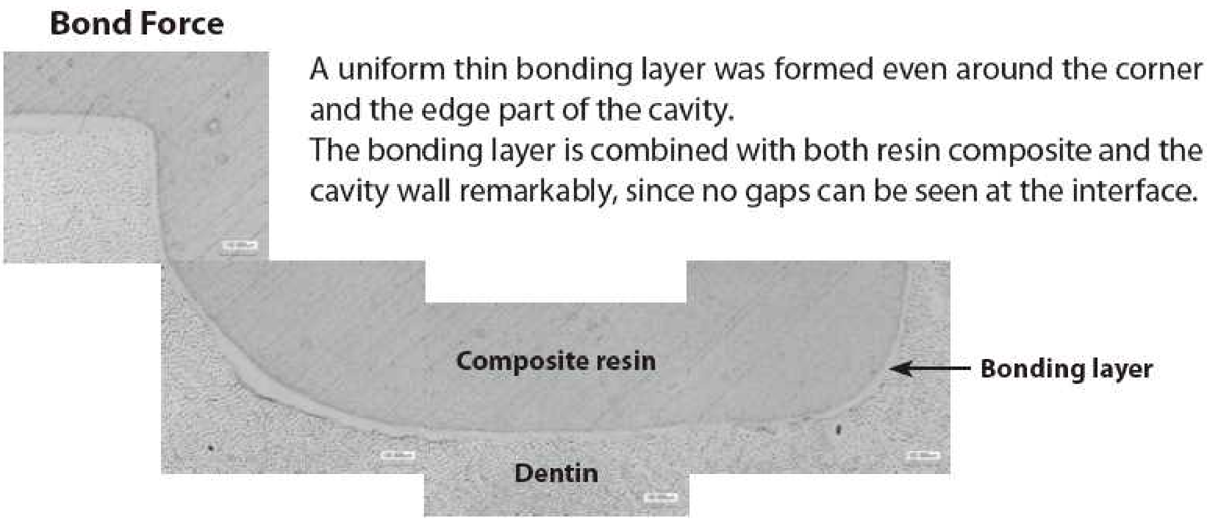


Figure 15 Adhesion interface (Bond Force)

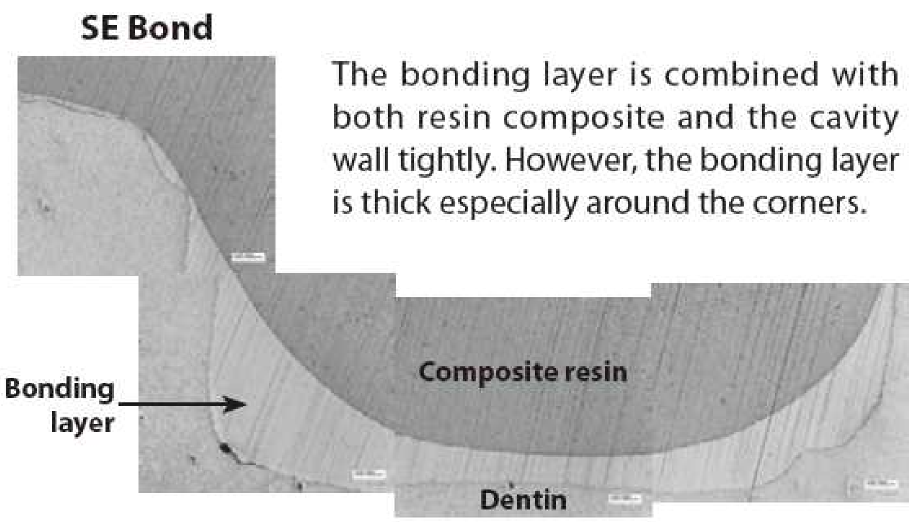


Figure 16 Adhesion interface (SE Bond)

G-Bond

The bonding layer is full of bubbles. The gaps appeared between bonding layer and dentin.

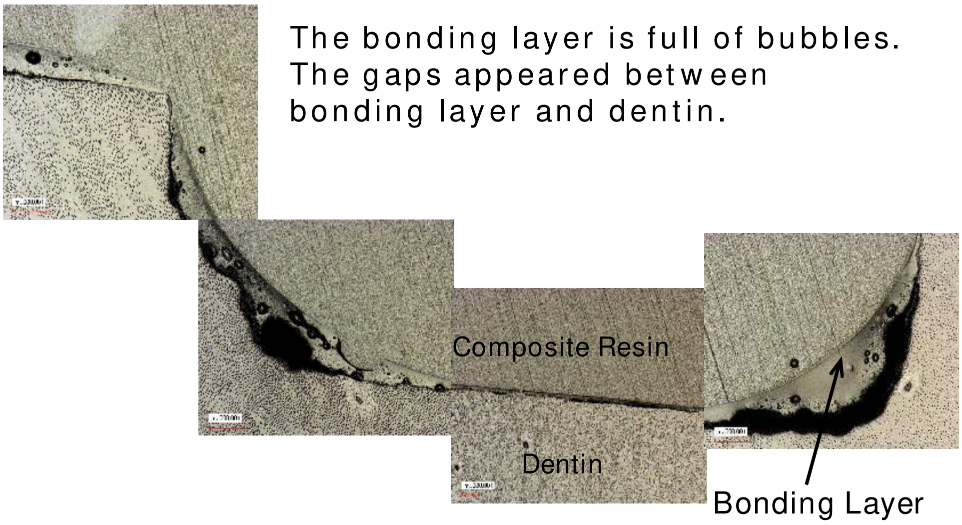


Figure 17 Adhesion interface (G-Bond)

Easy Bond

The bonding layer became thick around the corners. The gaps appeared between bonding layer and dentin.

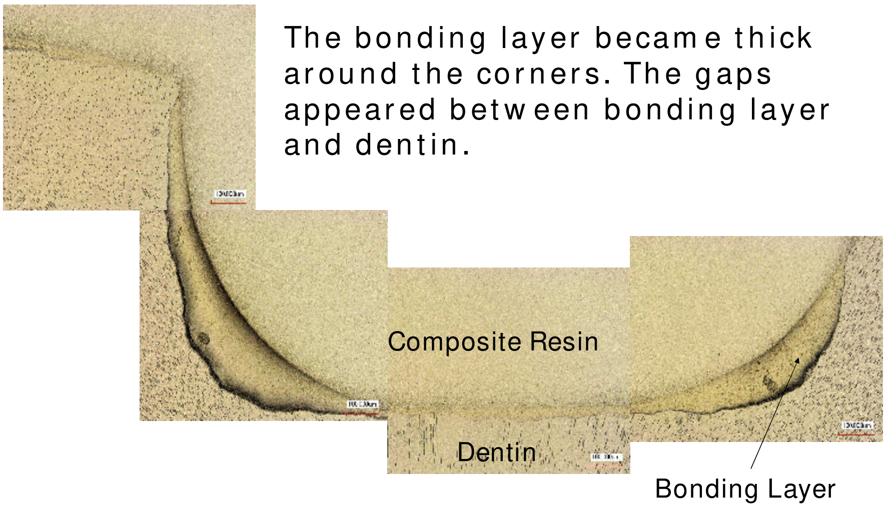


Figure 18 Adhesion interface (Easy Bond)

XenoV

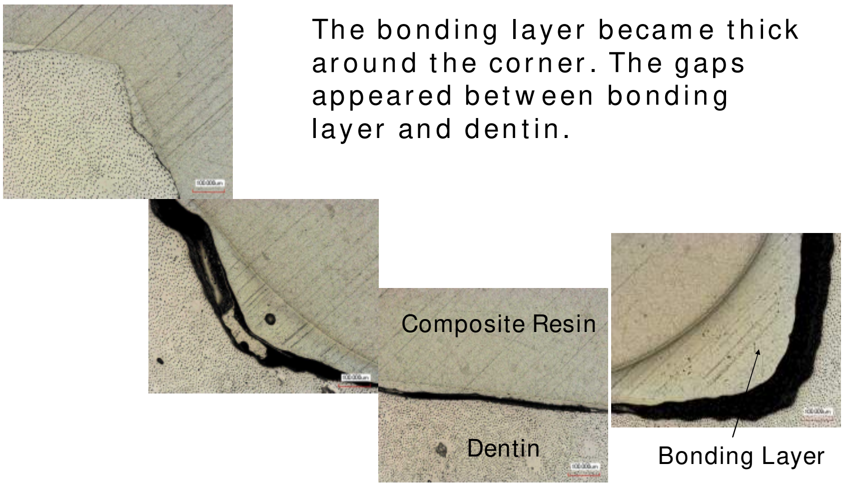


Figure 19 Adhesion interface (Xeno V)

OptiBond FL

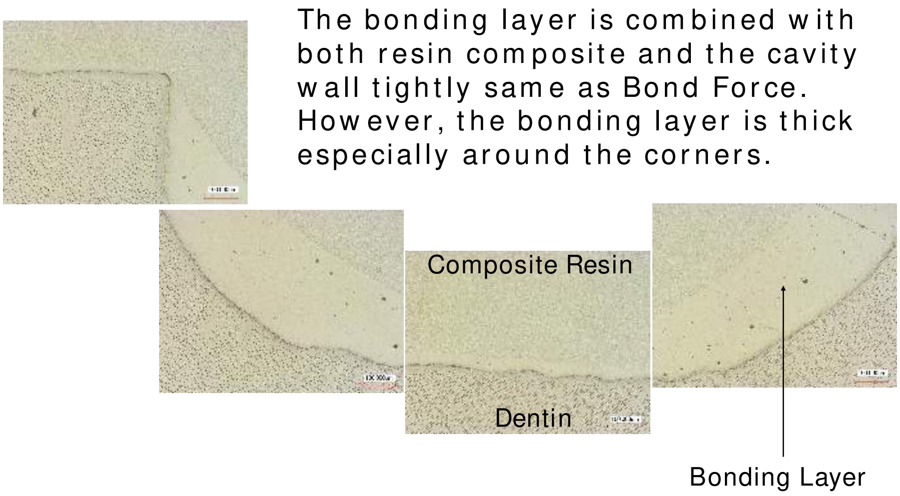


Figure 20 Adhesion interface (OptiBond FL)

Single Bond Plus

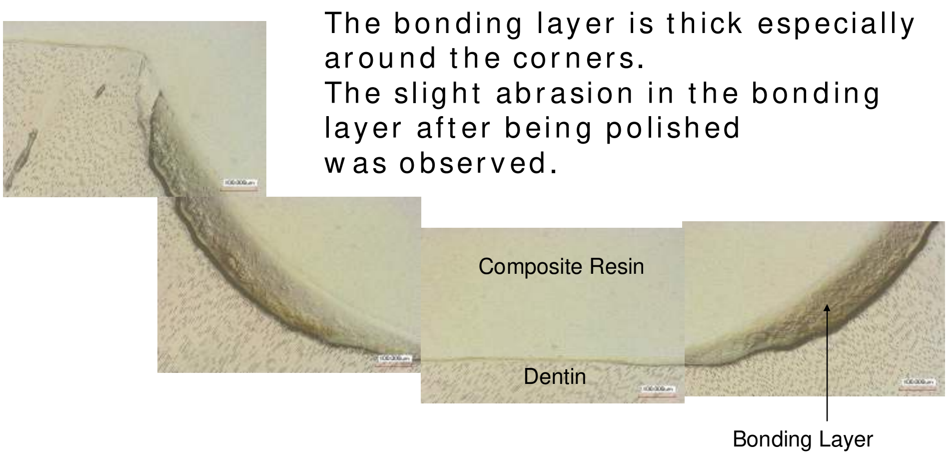


Figure 21 Adhesion interface (Single Bond plus)

Despite the excellent adhesion performance of Tokuyama Bond Force to dentin, the resin-impregnated layer is quite thin, as shown above. While good resin-impregnated layers had been attributable to the deep penetration of adhesive components into the dentin, another adhesion mechanism besides the formation of a favorable resin-impregnated layer appears to be at work with Tokuyama Bond Force.

The next Chapter describes in detail how Tokuyama Bond Force achieves high adhesion to dentin and enamel.

4. Adhesion mechanism

4.1 Adhesion mechanism of Tokuyama Bond Force

The composition of Tokuyama Bond Force is shown below:

- Adhesive SR (self-reinforcing) monomer
- Polymerizing monomer (HEMA, Bis-GMA, 3G)
- Water
- Alcohol
- Glass filler
- Photopolymerization catalyst

While Tokuyama Bond Force contains the phosphate monomer (PM) also used in One-Up Bond F, Tokuyama Bond Force differs from conventional one-step adhesives in that the PM self-organizes partly within the bonding material, as shown in Figure 22, forming multifunctional monomer structures (adhesive SR monomers) with several groups that polymerize with the phosphate groups interacting with residual tooth calcium and other monomers.

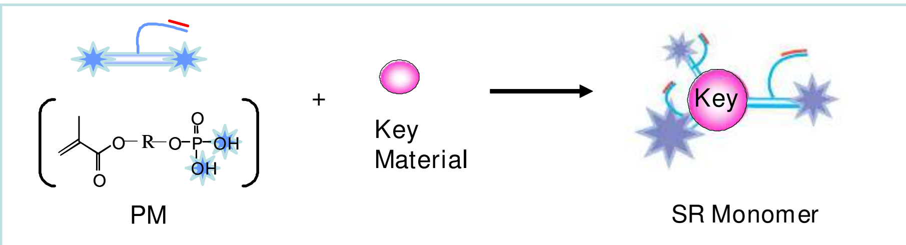


Figure 22 Adhesive SR monomer

As shown on the left in Figure 23, single-point interaction is considered as the key mechanism for interactions between tooth (calcium) and adhesive monomers used conventionally (PM, MAC-10, etc.). On the other hand, an adhesive SR monomer having several functional groups per molecule that interact with calcium is capable of interacting with tooth calcium at multiple points, as shown on the right side of Figure 23. This approach is believed to achieve higher binding with dentin/enamel at the molecular level when compared to existing one-step adhesives.

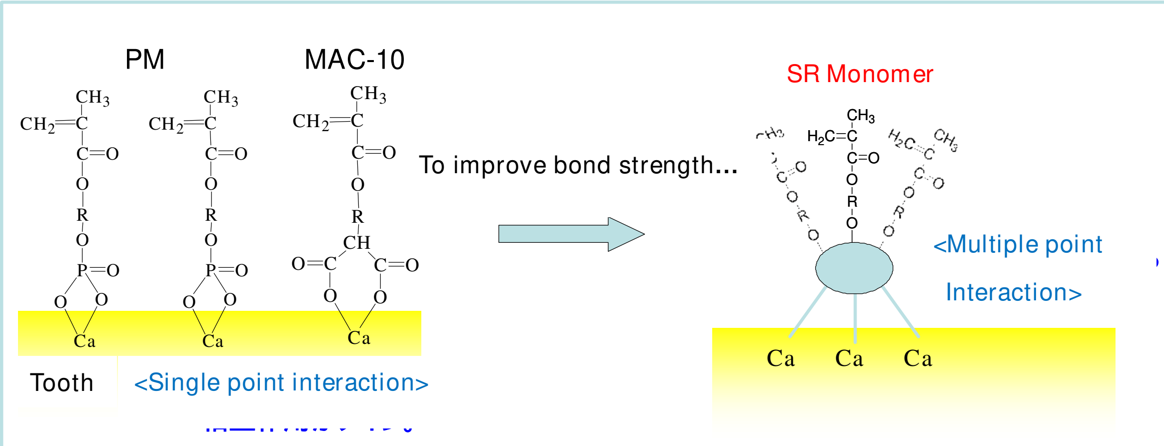


Figure 23　SR monomer interaction with tooth(calcium) at multiple point

In addition to the above-referenced interaction with dentin/enamel, the phosphate group of the adhesive SR monomer is capable of forming an ionic bond with calcium ions freed on the adhesion interface during tooth demineralization. The adhesive SR monomers concentrated on the adhesion interface by air-drying after application are capable of three-dimensional crosslinking involving calcium ions (Figure 24). That is, the additional phosphate groups provided by the Tokuyama Bond Force adhesive SR monomer (compared to conventional adhesive monomers) allows the formation of strong, insoluble adhesion layers on the adhesion interface due to three-dimensional crosslinking involving calcium ions, independent of self-polymerization before the bonding layer is light-cured. Since these crosslinking reactions form reliably regardless of the extent of air-drying after applying the bonding solution, the bond strength of Tokuyama Bond Force is less likely to be affected by the extent of air -drying following application, as discussed in Chapter 3-3.

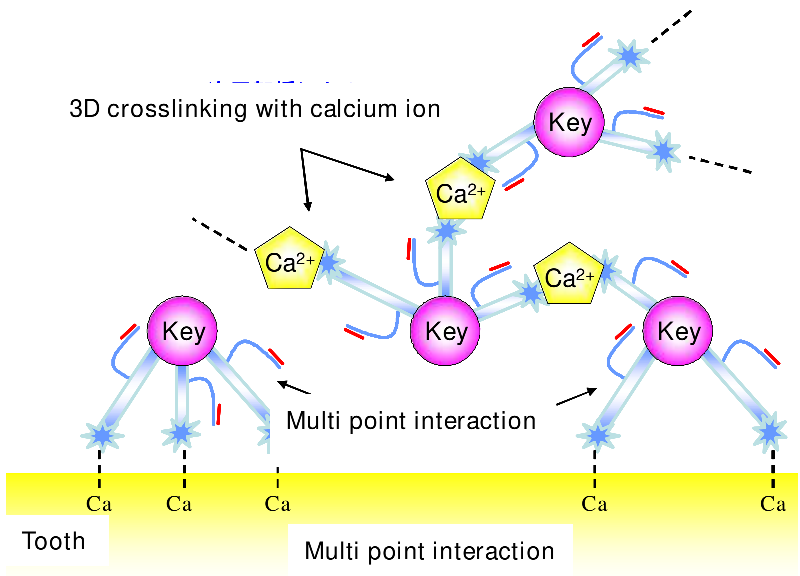


Figure 24　Three-Dimension closslinking reaction of SR Monomer to calcium ion

We performed the following test to confirm this hypothesis.

We confirmed the multiple-point interaction of the adhesive SR monomer in Tokuyama Bond Force with dentin/enamel and the insoluble layer formed by three-dimensional crosslinking reactions involving calcium ions by the following methods. Figures 25 and 26 show the results.

Test methods:

(1) We polished the surface of bovine tooth enamel with Emery paper (#600), and applied Tokuyama Bond Force. After the tooth was left to stand for 20 seconds, it was blow-dried at low pressure for 5 seconds and at medium pressure for 5 seconds.

(2) The tooth was soaked in ethanol without light curing and cleaned by ultrasound for 30 seconds.

(3) The tooth was dried and its treated surface analyzed by SEM.

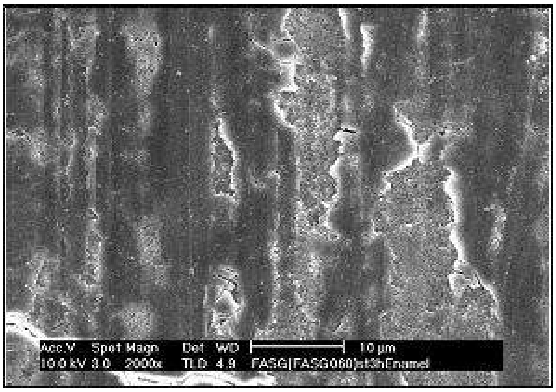


Figure 25 Bond Force treated surface

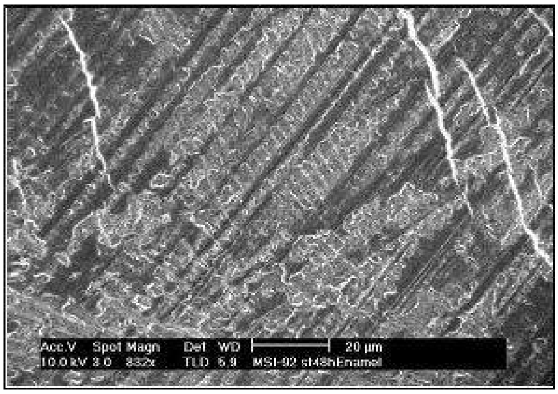


Figure 26 BF treated Surface (after polish)

Despite ultrasonic cleaning, a layer that appeared to be the bonding material clearly remained on the Bond Force-treated surface (Figure 25). Figure 26 shows an SEM image of the same surface polished using a scaler. Removing the surface over the layer believed to be the bonding layer revealed a normal demineralized enamel surface, suggesting that the layer on the tooth surface observed in Figure 25 is not a smear layer. For comparison, Figure 27 shows an SEM image in which the same observation was performed using the previous bonding material (One-Up Bond F Plus), which lacks the adhesive SR monomers but whose bonding layer is easily washed away by ultrasonic cleaning.

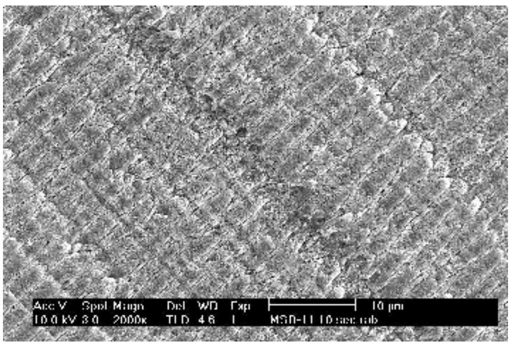


Figure 27 One-Up Bond treated surface

Next, the reaction behaviors of calcium ions and SR monomers included in Tokuyama Bond Force were confirmed by the following methods. Figures 28 and 29 show the results.

Test methods:

(1) Besides excluding the photopolymerization catalyst for preventing the bonding solution from curing due to photo polymerization, we prepared a bonding solution comparable to Tokuyama Bond Force (with the adhesive SR monomer).

(2) In addition to excluding the photo polymerization catalyst and the key materials for forming the SR monomers, we prepared a binding solution comparable to Tokuyama Bond Force (without the adhesive SR monomer).

(3) To the above two solutions, we added hydroxyapatite powder (15% wt of the total weight) and stirred for 5 minutes to recreate the conditions for dentin demineralization.

(4) After removing excessive hydroxyapatite powder by centrifugal filtration, we removed volatile organic solvents by blow-drying.

(5) We visually compared and analyzed the characteristics of each bonding solution.

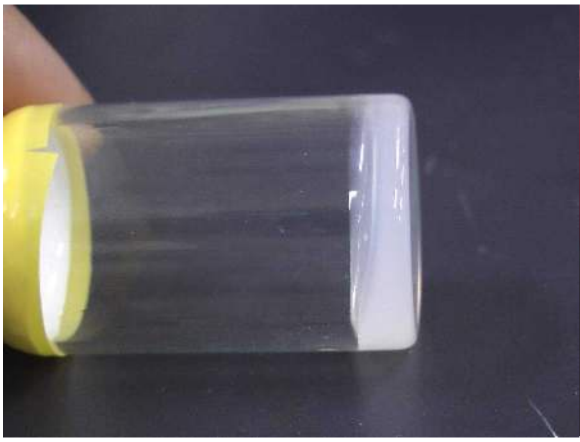


Figure 28　With SR Monomer

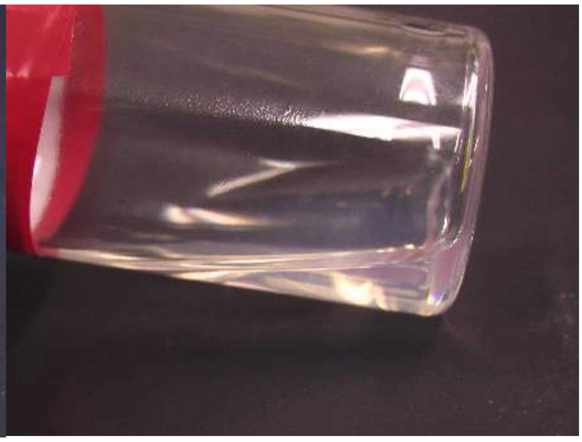


Figure 29　Without SR Monomer

When adding calcium ions to the system with the adhesive SR monomer, as shown in Figure 28, the bonding solution turned into agar due to three-dimensional crosslinking reactions between calcium ions and the adhesive SR monomers. But when we added calcium ions to the system without the adhesive SR monomer, the properties of the solution did not change significantly (Figure 29).

The results of the above two tests suggest that, when applying Tokuyama Bond Force containing the adhesive SR monomer to a tooth surface, a strong insoluble bonding layer forms due to: 1) multiple-point interactions of the adhesive SR monomer with dentin calcium; and 2) three dimensional crosslinking of the adhesive SR monomer and calcium ions.

A bonding layer is formed through multiple-point interactions and three-dimensional crosslinking of the adhesive SR monomer, and photo irradiation causes the layer to polymerize and cross-link with other monomers, resulting in even stronger curing. While existing adhesive monomers have only one polymerizable group, Tokuyama Bond Force's adhesive SR monomer has multiple polymerizable groups. In other words, adhesive monomers with one polymerizable group can only form a linear polymer like MMA monomers, while Bond Force adhesive SR monomers cross-link to form a three-dimensional mesh polymer, resulting in a strong hardened layer compared to existing monomers. Figure 30 shows the three-point bending strength of a cured Bond Force layer (after preparing and curing, the sample was soaked in 37 ˚C for 24 hours). Thanks to the SR monomer, the Bond Force physical strength clearly exceeded that of the existing one-step bonding materials and was comparable to that of SE Bond, a two-step bonding material. This is one of the reasons Tokuyama Bond Force, a one-bottle/one-step bonding material containing water and hydrophilic organic solvent, exhibits adhesion performance comparable or superior to two-step bonding materials.

* Bonding materials used in the bending test. BF: Bond Force, TS: Tri S Bond, OBFP: One-Up Bond F Plus, OP: OptiBond All-In-One, Xeno: XenoIV, iB: iBond, SE: SE Bond, MA: Mac-Bond II
* Measurement took place after soaking cured samples in 37˚C water for 24 hours.

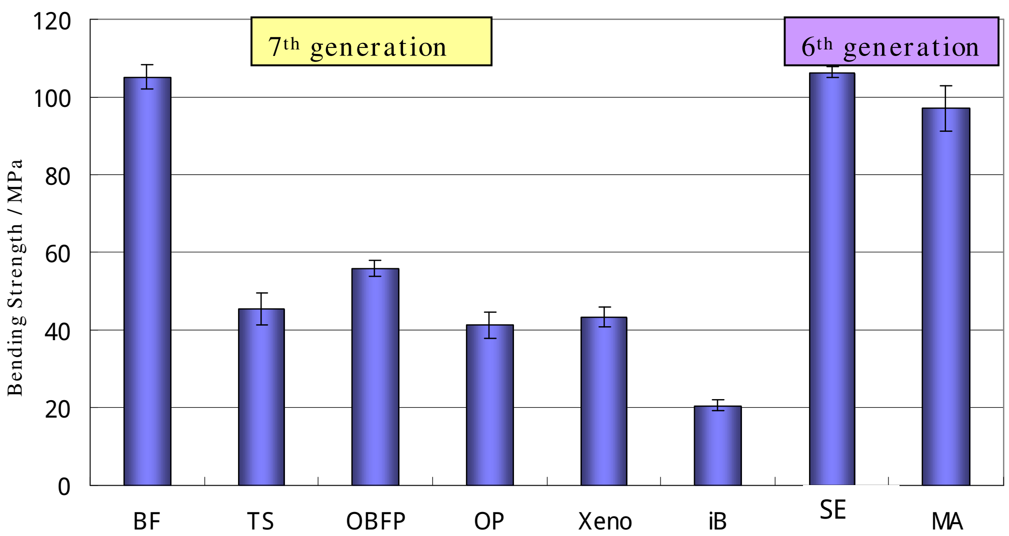


Figure 30 Bending strength

A study by Prof. Junji Tagami and DSr. Masatoshi Nakajima and others at Tokyo Medical and Dental University clarifies that the strength of cured Tokuyama Bond Force samples. Figure 31 shows the results of a tensile strength test for bonding materials cured in the shape of dumbbells. The tensile strength for Tokuyama Bond Force was significantly higher than for Tri S Bond.

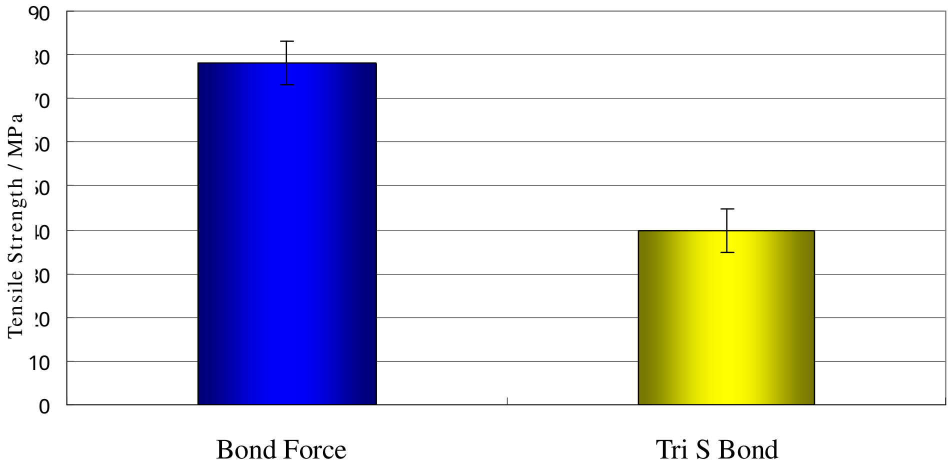


Figure 31　Tensile Strength

As mentioned above, the superior adhesion of Tokuyama Bond Force is attributable to: the improved binding force with dentin/enamel at the molecular level through multiple points of interaction; three-dimensional crosslinking of the adhesive SR monomer and calcium ions; and the formation of a highly water resistant adhesion layer by multifunctional polymerization crosslinking.

5　Other features

5-1 Working time

In general, one-bottle/one-step bonding materials contain volatile organic solvents. G-Bond and iBond contain highly volatile acetone. Once a certain amount of acetone evaporates, the water in the bonding material separates; that is, they are phase-separation bonding materials. Subsequently, once a bonding material is placed on a mixing dish, it must be used immediately. If the phase separation occurs, adhesion performance is significantly reduced. Hence, usage precautions are required. But with Tokuyama Bond Force, even if the volatile organic solvent evaporates completely, the bonding material does not undergo phase separation (Figure 32). It is, in short, a homogeneous bonding material. And because it uses an alcohol that is less volatile than acetone, once a drop of the bonding material is placed on a mixing dish, it is usable for 5 minutes, giving dentists extra time. Figure 33 shows the effects of time on adhesion strength of Tokuyama Bond Force after placing a drop of the bonding material on a mixing dish in a light-proof container.

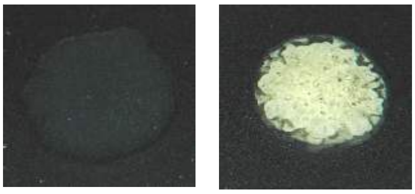


Figure 32 Phase separation
(1 min after dispense)

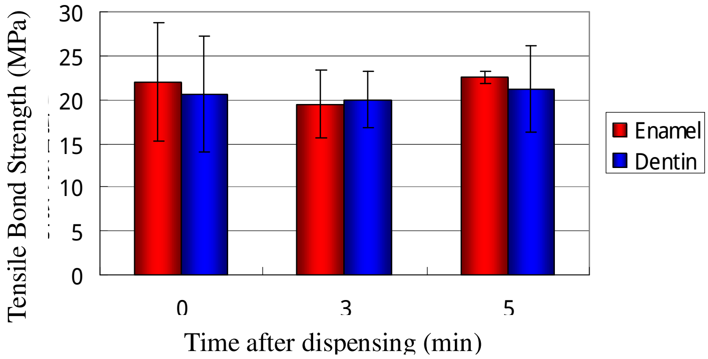


Figure 33 Effect of time on bond strength after dispensing
(Bond Force)

Even leaving a drop of Tokuyama Bond Force to stand in a mixing dish for 5 minutes does not affect bond strength. But after 5 minutes, the solvent evaporated, increasing viscosity and compromising usability.

5-2 Adhesion to uncut enamel (margin area)

MOD cavities were formed on human molars and were repaired using various bonding materials and composite resin (Estelite Σ Quick). After placing the molars in 37˚C water for 24 hours, we subjected the molars to repeat collision (load: 2 Kg, rate and count: 100 times/minute – 144,000 times/24 hours) and heat shock (4/60˚C thermal cycle 500 times) in 37˚C water. Then we soaked the molars in 0.1% concentration fuchsine solvent and left to stand at 37˚C for 24 hours. Using a diamond cutter, we cut each molar to allow analysis of marginal leakage in the occlusal and cervical areas. We assessed marginal leakage (pigment penetration) in the occlusal and cervical areas using the following criteria:

Assessment standards:
-: No pigment penetration,
+: Penetration into enamel,
++: Penetration into dentin,
+++: Penetration into cavity floor

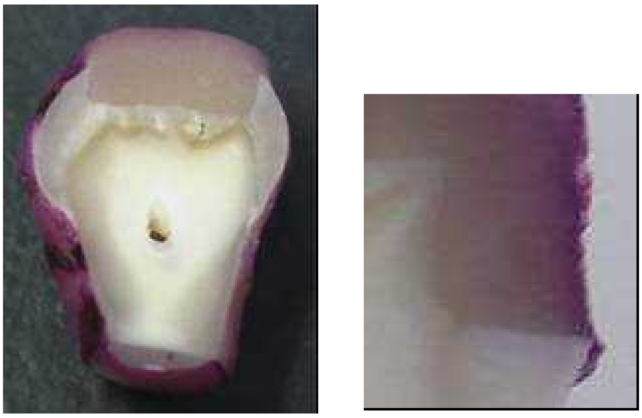
Table 4 summarizes the results. Figures 34-39 show the degree of pigment penetration for each sample.

Table 4 Degree of pigment penetration

Bonding Agent	Sample No.	Occlusal		Cervical	
Bond Force	1	−	−	−	−
BF	2	−	−	−	−
SE BOND	1	−	−	−	−
SE	2	−	−	−	−
Tri S Bond	1	+	+ +	+	+
TS	2	+	+	+	−
OptiBond AIO	1	+ +	+	−	−
OP	2	+	+	+	−
XenoIV	1	+ +	+	+	+
Xeno	2	+ +	+ +	+	+
iBond	1	+ + +	+ +	+ +	+ +
iB	2	+ +	+ + +	+ +	+ +

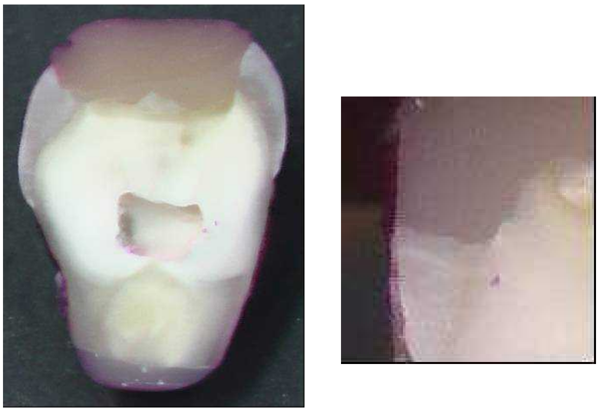
As shown above, the marginal sealing of Tokuyama Bond Force was comparable to two-step bonding materials, while pigment penetration was absent from both the crown and cervix areas.

As the result above, it is indicated that the adhesion of Tokuyama Bond Force to un-cut enamel(margin) is excellent.



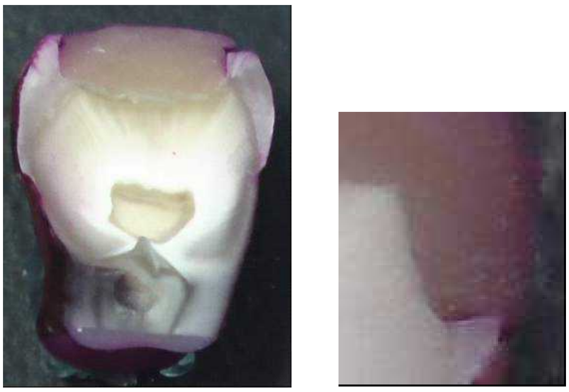
Marginal leakage on occlusal and cervical areas was NOT found.

Figure 34 Marginal Leakage of Bond Force



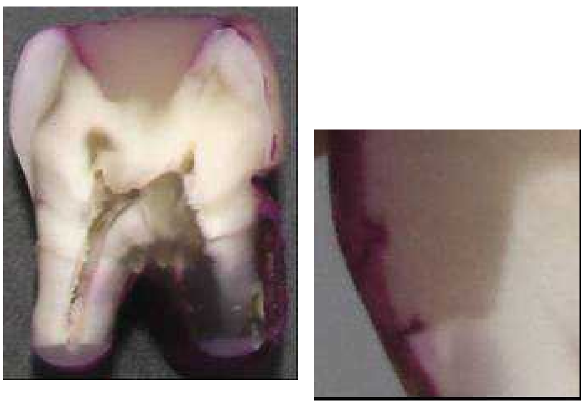
Marginal leakage on occlusal and cervical areas was NOT found.

Figure 35 Marginal Leakage of SE BOND



Marginal leakage on occlusal and cervical areas was found (to Enamel).

Figure 36 Marginal Leakage of Tri S Bond

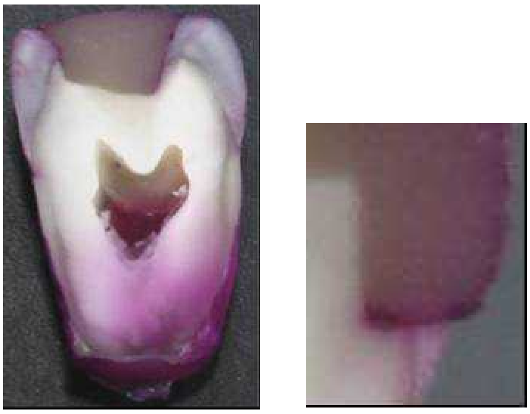


Marginal leakage on occlusal and cervical areas was found (to Dentin).

Figure 37 Marginal Leakage of OptiBond AIO

Marginal leakage on occlusal and cervical areas was found (to Dentin).

Figure 38 Marginal Leakage of XenoIV



Marginal leakage on occlusal and cervical areas was found (to the Cavity Floor).

Figure 39 Marginal Leakage of iBond

Dr. Blunck at Humboldt University of Berlin assessed adhesion to uncut enamel (margin) and obtained the following highly favorable results:

Assessment methods

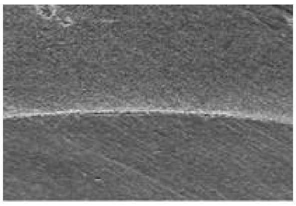
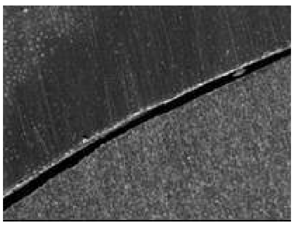
1) A class-V cavity (width: 3 mm, height: 4 mm, depth: 1.5 mm) was formed on the cervical region of a human premolar.

2) Using Tokuyama Bond Force, the cavity was filled with a composite resin (Estelite Σ).

3) The sample was left to stand in water for 21 days, then subjected to heat shock (5/55˚C for 2,000 times).

4) The sample was cut and the adhesion interface analyzed by SEM (x200). Adhesion was assessed and quantified by the following criteria:

●Criteria

Margin Quality		SEM Image
1	Margin is not found Gap is not found	
2	Margin is found clearly Gap is not found	
3	Gap is found Width of Leakage: within 2µm	
4	Gap is found Width of Leakage:over 2µm	

Figures 40 and 41 show the results. The figures represent the percentage of the margin quality of 1 with respect to the entire margin length.

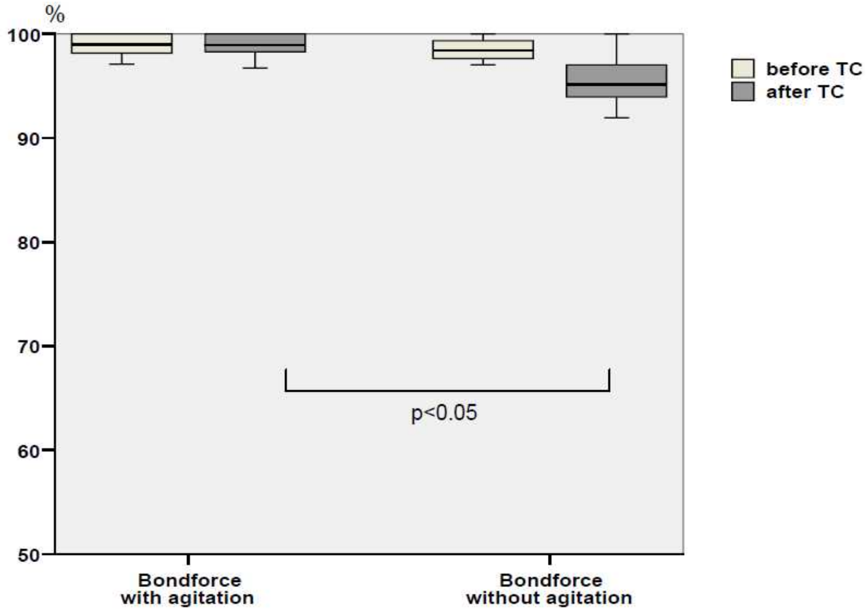
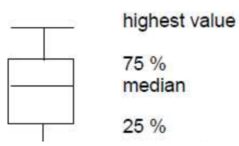


Figure 40 Amount of margin quality 1 in % of the entire margin length in **enamel** at Class V cavities for ***Bond Force*** with and without agitation before TC (TM 1) and after TC (TM2)



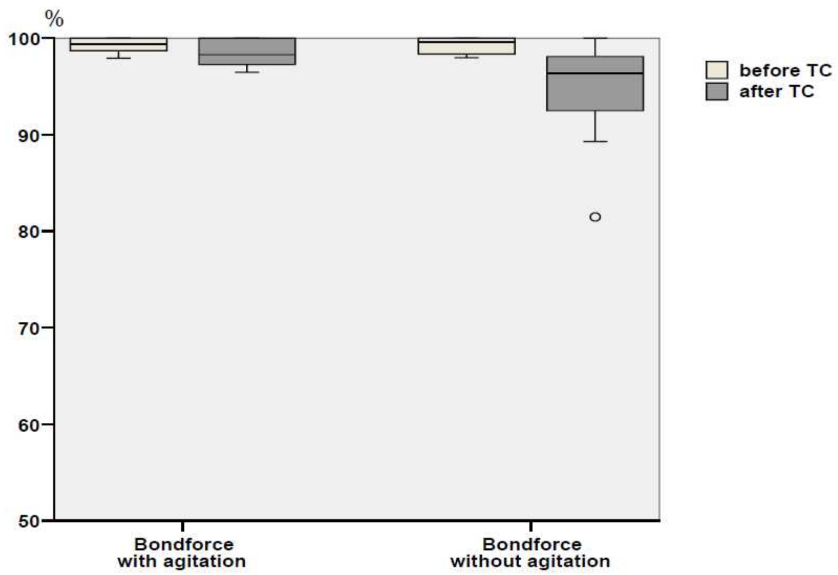


Figure 41 Amount of margin quality 1 in % of the entire margin length in **dentin** at Class V cavities for ***Bond Force*** with and without agitation before TC (TM 1) and after TC (TM2). (∗ = outlier)

As shown above, microleakage was generally absent in the adhesion interface (≥95-99%), indicating a high marginal match between the dentin and enamel. Also, a rubbing procedure performed while applying the bonding solution significantly improved endurance. Tokuyama Bond Force is a highly reliable bonding system that can be safely used for 20 seconds following application to uncut enamel by implementing rubbing with a microbrush.

5-3 Effects of tooth surface moisture

While the target tooth surface should ideally be dried before adhesion, in certain clinical settings, moisture often cannot be completely eliminated by air-drying. We assessed the effects of wetness (wet, damp, and dry) on bond strength as described below. Figures 42 and 43 show the results.

Dry: Air-dried tooth surface

Moisture: Damp tooth surface (left to stand for 1 hour in the hot layer at 37˚C at 100% humidity)

Wet: Tooth surface with water droplets

* Bonding materials used in the test. BF: Bond Force, TS: Tri S Bond, BG: G-Bond, Xeno: XenoIV, iB: iBond, OP: OptiBond All-In-One

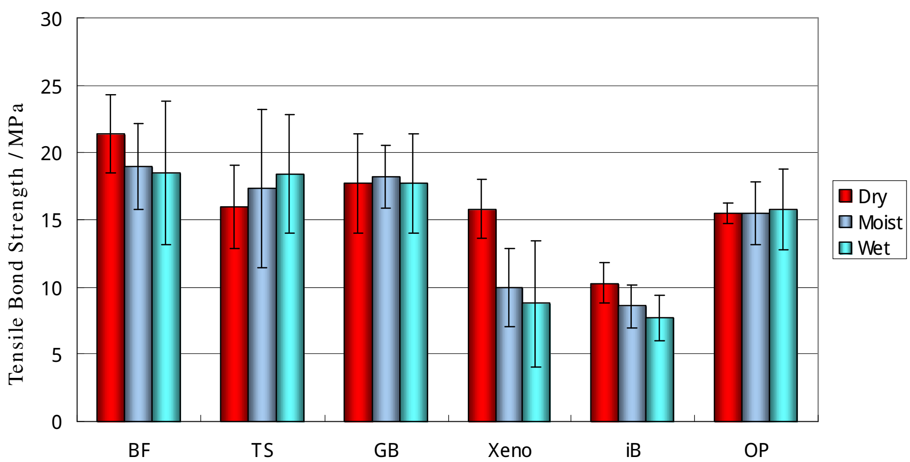


Figure 42 Effect of tooth surface moisture (enamel)

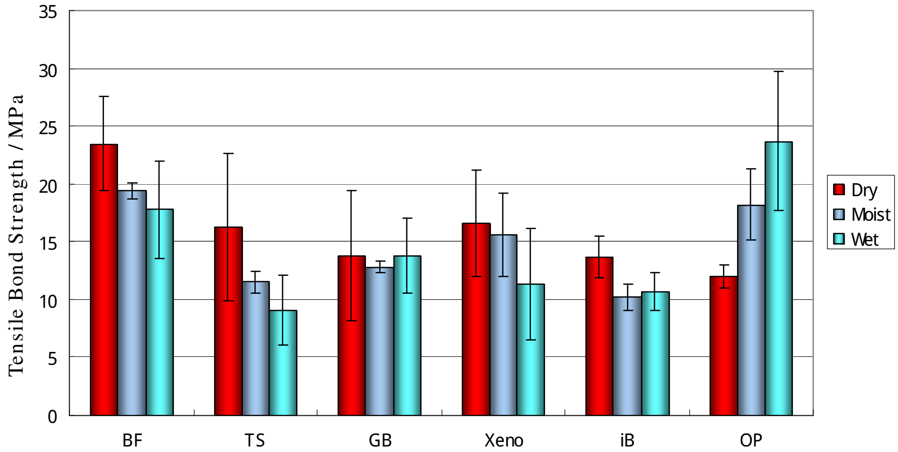


Figure 43 Effect of tooth surface moisture (Dentin)

With Tokuyama Bond Force, bond strength to dentin indicated a slight downward tendency when wet (when water droplets were present on the surface), but not at clinically compromising levels. Bond strength was virtually unaffected when moist (but without water droplets). The bond strength of TS and Xeno was reduced when wet and that of OP when dry. Thus, Tokuyama Bond Force is less likely to be affected by the moisture status of tooth surfaces.

5-4 Adhesion to various light-cured composite resins

Figure 44 compares adhesion to various commercially available light-cured composite resins.

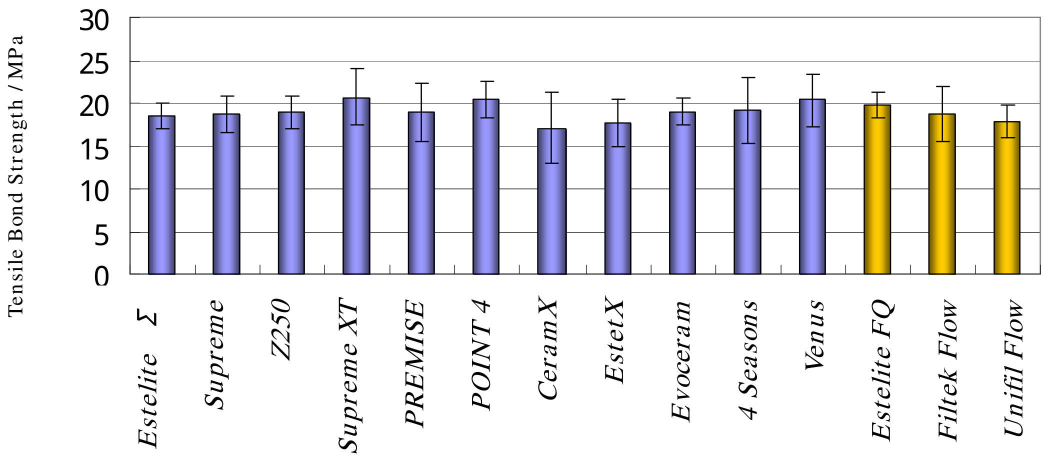


Figure 44 Bond Strength to various composite resin

Favorable adhesion was achieved with all composite resins, indicating Tokuyama Bond Force's compatibility with all composite resins.

5-5 Sustained fluoride release

Tokuyama Bond Force releases fluoride gradually. Sustained fluoride release was assessed for Tokuyama Bond Force. Figure 45 shows the results.

Test methods:

1) Into a polyacetal mold with a diameter of 15 mm and a thickness of 0.5 mm, we poured a bonding material, then irradiated light for 30 seconds from each side to prepare a cured sample. The sample was then stored in 10 ml of distilled water at 37˚C.

2) After a certain period of storage, we measured the amount of released fluoride by ion chromatography (DX-120: Dionex Inc.). The measurement conditions were as follows:

(Detector: electric conductivity detector, Column: IonPac AG14/AS14, Eluate: 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$).

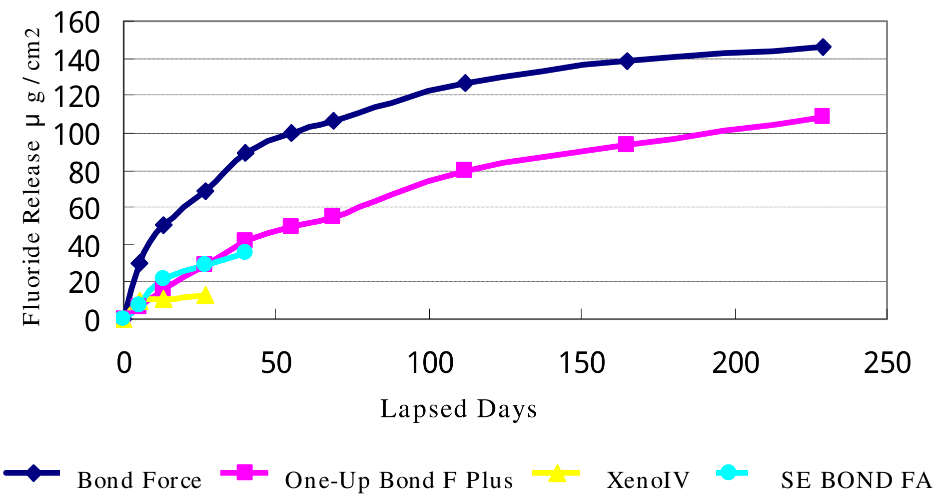


Figure 45 Fluoride Release

The volume of sustained fluoride release for Tokuyama Bond Force was about twice that of One-Up Bond F Plus and highest among all commercially-available bonding materials with sustained fluoride release.

6. Usage precautions

While Tokuyama Bond Force offers superior adhesion performance, its adhesion performance cannot be fully expressed under several conditions. This chapter discusses usage precautions for Tokuyama Bond Force.

6-1 Adhesion to self-cure/dual-cure composite resin

Root canal therapy uses dual-cure composite resins. Table 5 shows the results of an adhesion test using Tokuyama Bond Force and dual-cure composite resins. A tooth surface was treated using Tokuyama Bond Force and a dual-cure composite resin applied and cured by chemical polymerization. The results confirmed adhesion failure due to negation by the acid monomer in the bonding material of the action of the polymerization catalyst (amine) in the composite resin. Favorable adhesion can be achieved by light curing dual-cure composite resins.

Table 5 Adhesion test using Tokuyama Bond Force and self-cure/dual-cure composite resins

Run	Composite	Cure type	Bond Strength to Dentin / MPa (S.D.)
1	DC Core (Kuraray)	Self	3.0(0.2)
		Light	20.0(1.6)
2	Unifil Core (GC)	Self	6.4(3.2)
		Light	21.5(1.8)

※ Bond Force is light cured

This means that Tokuyama Bond Force cannot be used in patients if a dual-cure composite resin is required to be cured chemically.

6-2 Effects of various medicaments

Because the medicaments listed in Table 6 affect dentin adhesion, as shown in Figure 46, they must not be used with Tokuyama Bond Force.

Table 6 Medicaments with influence on adhesion

Product	Use
Diammine Silver Fluoride	Caries Depressant, Pulp Canal Antiseptic, Pulp Canal Cleaning
Hydrogen Peroxide (Oxidol)	Antiseptic、Cleaning
Sodium Hypochlorite	Pulp Canal Antiseptic, Pulp Canal Cleaning
Eugenol	Temporary filling material, Temporary Cement, Pulp Protection Material

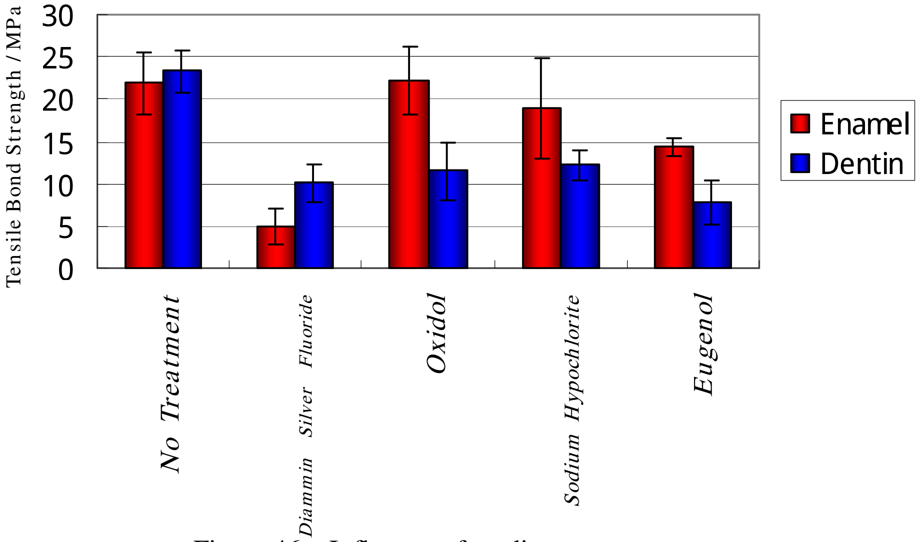


Figure 46　Influence of medicaments

7. Frequently Asked Questions

Q1. How many drops can I dispense per one bottle or one pen?

A1. Approximately 320 drops per one bottle (5mL), 190 drops per one pen (2mL)

Q2. Do I need to shake the bottle before use?

A2. No.

Q3. What is pH of Tokuyama Bond Force?

A3. Around 2.3

Q4. How long can I use Tokuyama Bond Force after dispensing on the dish?

A4. Complete the application within 5 minutes after dispensing because Tokuyama Bond Force contains a volatile alcohol as a solvent.

Q5. What if Tokuyama Bond Force dropped on the mucosal membrane?

A5. Wipe the affected area immediately. And thoroughly flush with water after restoration. Affected areas may whiten due to protein coagulation but will disappear within 24 hours.

Q6. What is shelf life of Bond Force?

A6. 3 years after the date of production under refrigeration.

Q7. Does Tokuyama Bond Force have fluoride release?

A7. Yes.

Q8. Will the liquid of Tokuyama Bond Force cause phase separation?

A8. No, Tokuyama Bond Force will not cause phase separation even if the solvent (alcohol) is evaporated because Tokuyama Bond Force contains hydroxyethyl methacrylate (HEMA) which is relatively hydrophilic and improve compatibility between water and monomer.

Q9. Is there any risk that HEMA may reduce water resistance of bonding layer, thereby cause less bonding strength and durability?

A9. That risk is minimized by the best balance of the composition contained in Tokuyama Bond Force. Besides, SR monomer employed in Tokuyama Bond Force, which forms cross-link resin matrix, contributes to enhance physical properties of bonding layer as well as adhesive strength and durability as explained in this report.

8. Conclusions

Commercially introduced in February 2007, Tokuyama Bond Force is capable of forming stronger, more water resistant bonding layers than existing one-step bonding materials due to multiple point interactions between the adhesive SR monomer and dentin surface calcium (ions) as well as three-dimensional crosslinking reactions between the adhesive SR monomer and calcium ions eluted during demineralization.

Although a one-solution one-step bonding material, due to the above-mentioned adhesive SR monomer, Tokuyama Bond Force offers bond strength comparable or superior to two-step bonding materials. It represents a revolutionary bonding material with lower sensitivity to air-drying with notable promise for clinical settings.

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Physical Properties

	Tensile Bond Strength (MPa)								Bending Strength
	Enamel				Dentin				
	24h	S.D.	TC3000	S.D	24h	S.D	TC3000	S.D.	
Tokuyama® Bond Force	21.9	3.6	19.9	5.4	23.3	2.5	20.5	5.5	105.2
Clearfil™ Tri-S Bond	13.8	3.5	7.0	3.0	15.7	3.3	10.1	3.0	45.3
G-Bond™	18.0	2.6	9.0	5.6	14.0	2.8	5.7	3.7	N/A
Xeno® IV	15.8	2.2	13.1	3.6	16.6	4.6	13.3	2.7	43.3
Xeno® V	12.4	3.3	3.2	2.4	9.3	2.8	2.4	2.3	N/A
iBond®	10.3	1.5	1.7	0.8	13.7	1.8	8.6	2.9	20.5
OptiBond® All-In-One	15.5	0.8	11.8	2.0	12.0	1.0	12.7	0.7	N/A
Adper™ Easy Bond	13.8	5.3	9.3	5.4	21.4	6.7	13.7	8.2	N/A
Clearfil™ SE-Bond	21.2	2.6	18.4	3.9	22.6	2.5	17.3	4.1	106.4
Adper™ Prompt™ L-Pop™	9.4	5.4	0.6	0.1	8.2	4.3	0.5	0.3	N/A
Adper™ Single Bond Plus	19.0	6.2	15.4	2.2	8.7	5.2	7.9	3.3	N/A
Prime&Bond® NT	16.6	5.6	11.6	2.2	0.0	0.0	0.0	0.0	N/A
OptiBond® Solo Plus	22.8	3.6	N/A	N/A	18.9	2.0	N/A	N/A	N/A

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