Brand-New SE for you

CLEARFIL™ LINER BOND F
2-Step Self-Etching Adhesive

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- Read the Instruction for Use supplied with the products before use.
- The specifications and appearance of the product are subject to change without notice.
Introduction

Many of the basic principles for restorative techniques since the era of G.V. Black are being reexamined and at present, the philosophy of restorative techniques has changed to Minimal Intervention Dentistry, which is a minimally invasive operative approach for treatment of cavitated lesions or healing the non-cavitated lesion. Adhesive materials have made this philosophical change possible.

Kuraray Company (Kuraray Noritake Dental Inc., Japan) has played a major role in adhesive resin material development and it is impossible to say that its history of material development describes some of the major focal and transition points of adhesive resin restorations. The current worldwide prosperity of adhesive dentistry can be attributed to the great efforts of Kuraray and its staff. In addition, researchers have received great support from Kuraray, and have been guided by the great foresight, abilities and actions of the late Prof Eiichi Masuhara and Prof Takao Fusayama, both who helped pave the way towards adhesive dentistry.

1. Adhesive Resin Development and Transition

- Phosphoric Acid Total Etching (Etch and rinse adhesive systems)
  The history of adhesive resin composite restorative material development in Kuraray Noritake Dental Inc. began in 1978 with CLEARFIL BOND SYSTEM (Fig 1). This was the world’s first total-etch system, in which a solution of phosphoric acid was applied to enamel and dentin simultaneously. Phenyl-P (Fig 2) was used as the adhesive resin monomer. Adhesion to dentin by phosphoric acid etching had not previously been widely recognized internationally. It was only after the 1990’s that this system became well known and accepted even in western countries.
  Later, MDP was developed as a replacement for Phenyl-P, and CLEARFIL NEW BOND was created (Fig 3). After that, with the introduction of catalysts for visible light curing, CLEARFIL PHOTO BOND (Fig 4) was created. Each time adhesive systems were modified, the adhesion to dentin continued to improve (Fig 5).
- Primer Development
  In the 1980’s, the hybrid layer, first described by Prof Nobuo Nakabayashi, began to become better understood, and a lot of research has been performed to better determine adhesive mechanisms. Primers, which are important for promoting good dentin adhesion were invented and introduced, and under the guidance of Prof Hiroyasu Hosoda and his group. The outcome of their research was the introduction of the CLEARFIL LINER BOND SYSTEM (Fig 6).

Phosphoric acid etching of dentin was not accepted by western dental associations at this time. CLEARFIL LINER BOND SYSTEM used 10% citric acid containing 20% calcium chloride as a substitute for phosphoric acid as an etching agent to reduce the damage that occurs from phosphoric acid etching to dentin collagen fibrils. In addition, a primer was introduced in this adhesive system, which was shown to dramatically improve adhesion to dentin.

One very important research finding was that after washing and drying etched dentin, the surface collagen network shrank, and affected the infiltration of bonding resin; however, when the primer was used, it moistened and helped reopen the collagen network and promoted the infiltration of resin. This resulted in a remarkable increase in bond strength (Fig 7).

This product also contained a low viscosity resin composite, similar to a flowable composite resin, CLEARFIL LINER BOND PROTECT LINER. Applying this low viscosity resin composite after bonding procedures also improved adhesive ability.

This system showed the importance and effects of controlling bonding polymerization, but also resin wettability, and the importance of a low elastic modulus layer at adhesive interfaces to prevent gaps forming between a cavity surface and the resin restoration.

Interestingly, CLEARFIL LINER BOND SYSTEM exhibited the best clinical performance in a study evaluating the retention of the restoration in non-cavitous cervical lesions after 13 years. The retention rate was nearly 75%, though the other 12 adhesives exhibited the retention rates varying from about 65% to 5% (Fig 8). It is speculated that the reason for the best performance of CLEARFIL LINER BOND SYSTEM is not simply the bond strength of the material but also by the low viscosity resin. The
application of a low viscosity resin is believed to improve the bonding and adaptation of the composite at the cavity floor of the dentin by compensating the shrinkage stress of the composite.

2. Self-etching Primer Development

Adhesive resin monomers, such as Phenyl-P, MDP, or 4-META (Fig 2) are acidic monomers that contain either carboxylate or phosphate groups in the monomer molecule. Acidity of a monomer can affect polymerization, but these acidic groups are necessary for the adhesion to tooth substrates of these resin-based adhesives.

With the great efforts of corporate R&D, an epoch-making technique of “self-etching primer” was introduced to the dental profession in 1993. The very first products using this method from the Kuraray Company were CLEARFIL LINER BOND 2 (Fig 9) and PANAVIA 21 resin luting cement.

Due to the improved dentin bond strength of most of the adhesives in the 1990’s, conventional methods could not precisely evaluate the adhesive strengths. As a result, a new testing method: micro tensile bond test was developed – – , which enabled bond strength evaluation to become much more accurate by minimizing the adherent areas, as well as see the effects of bonding to all parts of normal and caries-affected dentin.

The next development of self-etching systems was CLEARFIL LINER BOND 2V (Fig 10), in which self-etching primer components were changed and polymerization was improved. In 1999, CLEARFIL SE BOND (Fig 11), consisting of one-bottle self-etching primer and one-bottle of light-cured bond was invented. In these 2-step self-etching type adhesives by Kuraray Noritake Dental Inc., the filled bonding resin is incorporated. Due to the filler particles in the bonding resin, the thickness of the bond layer tended to be thicker. A thick bond layer is considered to be effective to prevent the gap at the cavity floor as well as the use of the low viscosity resin of CLEARFIL LINER BOND.

In Japan, self-etching primers now have more than 20-years of clinical history. Apprehensiveness towards potentially deficient enamel etching has all but been solved and has shown to be clinically reliable. For those cases of uncut enamel or fluorosed enamel, then a brief application of phosphoric acid etching.

This led to much more information into the hybridized dentin formation mechanism and the fact that the use of self-etching primer on the collagen could be obtained without water-spray. Other research showed how to prevent collagen network shrinkage to form an adequate bond strength even when treated with phosphoric acid etching. It was important to keep dentin “wet”. Under these circumstances, wet bonding and moist bonding techniques were proposed – – . With those techniques, phosphoric acid etching to dentin was finally recognized in western countries. However, it was obvious that redundant water on the dentin surface inhibits effective bonding. Much discussion occurred about how much water was necessary to ensure a good bond. In Japan, however, self-etching primer systems had already widely spread into clinical practice, and the wet bonding technique was rarely used clinically.

What is important for adhesion to dentin is the infiltration of adhesive resin monomers which have excellent adhesion properties to tooth structure, particularly dentin, as well as adequate polymerization. For good resin infiltration, an acidic treatment with either phosphoric acid or self-etching primer is necessary to dissolve the smear layer that is produced on a tooth surface during dental cutting procedures. Regions produced after acid treatment, in other words, demineralized areas, even if only slight, must be hardened and protected by bonding resin infiltration. If not, the areas devoid of resin at the adhesive interfaces will affect the long-term durability of the bond.

The investigation of small voids and defects at the dentin adhesive interfaces can evaluate the quality of the bonding system used. Silver particles from a silver nitrate solution can infiltrate into dentin adhesive interface can reveal these subtle voids. The results for CLEARFIL SE BOND, using this above method showed no silver particles at the adhesive interface as shown in Figure 12. This result showed CLEARFIL SE BOND was able to achieve consecutive infiltration and polymerization of into tooth substances – – .

Figure 13 shows the adhesive interface between bonding resin and dentin treated with phosphoric acid etching. After phosphoric acid etching, wet bonding technique was used. Observation of this adhesive interface showed silver particles penetrated into both the bonding resin layer and hybrid layer. This revealed the existence of subtle voids where silver nitrate solution could infiltrate into the bonding resin layer itself as well as within the hybrid layer. These subtle defects in the bonding layer were caused mainly by residual water from the wet bonding technique. It seems this residual water from wet bonding might have the same affect on the hybrid layer. Silver particles were observed at the bottom of the hybrid layer,
which shows bonding resin infiltration was insufficient in this area even though collagen fibrils were exposed by phosphoric acid etch demineralization.

Water can also easily penetrate as well as silver nitrate in this area. Substances which damage collagen are also able to penetrate. In such circumstances, collagen and/or bonding resin degradation can occur easily, and failure of the adhesive interface is suspected to occur soon after bonding.

It was reported that compared with the self-etching systems, strong acidic treatment like phosphoric acid etching decreased bond strength significantly in evaluation of adhesion to dentin long-term durability.

As mentioned above, phosphoric acid etching to dentin adhesion creates structural defects, that is to say, layers of exposed denatured collagen in the adhesive interface, where bonding resin cannot infiltrate (Fig 14).

It can be concluded that the dentin bonding with the etch and rinse technique was obtained with the hybrid dentin, which is recognized as the micro mechanical retention with easily degenerated structural characteristics.

On the other hand, CLEARFIL SE BOND does not create such structural defects. Successive interfacial structures formed from resin composite, bonding resin, and the hybrid layer to dentin where etching effects do not reach (Fig 15).

In addition, analyses of the adhesive interfacial structure between dentin and resin revealed that acid- and base-resistant zones exist in the bonded dentin directly beneath the adhesive interface (Fig 16). This is referred to as the acid-base resistant zone. This zone is an area superior to original dentin properties, and has been called “Super Dentin”. It is anticipated this modification to the dentin will eventually become a new approach in prevention and protection against cavities damage of tooth structure (Fig 16) (6-8).

Needless to say, in an etch and rinse adhesive system using phosphoric acid etching, bonding resin cannot infiltrate well enough to allow the formation of Super Dentin. Super Dentin seems to be a unique interfacial structure created by bonding materials using the self-etching technique (6).

At present, the mechanism is continuing to be researched; however, it is known that the thickness and properties of Super Dentin layers do differ depending on the bonding system used. In cases where the adhesive materials with MDP as the adhesive resin monomer were used, Super Dentin formation was demonstrated very effectively (6-8). The MDP was also confirmed to react with the hydroxyapatite in a very short period, creating the stable salt when compared with the other adhesive monomers (6).

The result indicates MDP may have modified the components in dentin chemically, contributing to the creation of the Super Dentin.

4. Golden standard of the adhesive

It is obvious that the 2-step self-etching material with excellent functional adhesive resin monomer such as MDP is the most reliable and excellent adhesive. The analysis of numerous numbers of papers on the bond strength tests of adhesive resin materials also demonstrated that CLEARFIL SE BOND was the best in any kind of bond test results (Fig 17) (6).

When consider the dentin bond durability, quality and the stability of the hybrid layer, the dentin bonding mechanism in CLEARFIL SE BOND is completely different than those of etch and rinse adhesive materials. The concept of the bonding must be changed from the micro mechanical bonding with hybrid layer to the chemical bonding with the Super Dentin. From the viewpoint of dentin bond strength and bond durability, CLEARFIL SE BOND secures the conditions which make it the gold standard of the adhesive.

5. CLEARFIL PROTECT BOND and CLEARFIL LINER BOND F

More than 10 years of clinical evidence has not demonstrated any specific problems for the clinical durability of CLEARFIL SE BOND adhesion. There are several other shorter clinical trials which have also demonstrated its clinical success (6-8), however, time-dependent decrease in dentin adhesion was reported in all adhesive systems.

Though the decrease was subtle compared with an etch and rinse system using phosphoric acid, CLEARFIL SE BOND is no exception. Improvements in adhesive durability; however, were expected for CLEARFIL LINER BOND F (Fig 18) and CLEARFIL PROTECT BOND (Fig 19) due to their fluoride-releasing effect. Indeed, its long-term adhesive durability has greatly improved.

According to our previous study, the fluoride-containing bonding resin remarkably improved the durability of dentin bonding. Under the experimental design to intentionally accelerate the degradation of dentin bonding, even CLEARFIL SE BOND showed a decrease in bond strength after storage in water for 3 and 6 months, respectively. However, the fluoride-containing bonding resin maintained the initial bond strength when tested with the same self-etching primer (Fig 20).

One of the major cause of decrease in bond strength is considered to be the degradation of organic component of dentin at the bonding interface. The fluoride released from the fluoride-containing adhesive at the bonding interface was considered to have inhibited the enzymes (i.e. MMPs) from attacking the components of the bonding interface including the hybrid layer. The fluoride also has possibility of preventing the enzymes from being released from the mineralized matrix due to its remineralization action (6).

Regarding to the creation of Super Dentin, among current bonding agents, CLEARFIL LINER BOND F creates the thicker Super Dentin than CLEARFIL SE BOND even after the acid-base challenges (Fig 21, 22). Thickening the Super Dentin layer leads to the strengthening of teeth greater than their natural or original state. This is likely to become a new dental treatment to maintain sound teeth, particularly with regard to our aging population who will keep their teeth longer.

As adhesive resin enters a new era, it will not only serve as a restorative material, but also act as a functional material to protect teeth. Strengthening teeth, preventing caries, and improving the oral environment will also become possible (6-8).

6. Characteristics of All-in-one Systems and Bonding

With the increased spread of self-etching techniques and materials, current developments in the all-in-one or one-step bonding agents has rapidly occurred and become popular.

The adhesive mechanism of the all-in-one systems is very similar to the two-step self-etch systems. However, to add a self-etching
function to the bonding agent as a single step adhesive, a small amount of water must be added. The water is needed to maintain the etching function of the all-in-one bonding system. But it is also known that the presence of water is not good for bonding resin layer.

To circumvent this contradiuction, use an the air-drying method after the self-etching function of the all-in-one system and prior to light-curing. This should be done carefully and is specific to each product.

Generally, the composition needs a cocktail of resins that comprise an acidic adhesive resin monomer, a hydrophilic resin monomer (HEMA, etc) to ensure etching and resin infiltration steps into the tooth structure, and a hydrophobic resin monomer ( Bis-GMA, TEGDMA, etc) to stabilize the bond and link to the resin composite filling material. Then to maintain this combination of resin monomers in a fluid state a solvent (acetone, ethanol, etc) must be added, in addition to water to maintain a low pH and the polymerization catalyst system (Table 2).

As all-in-one adhesives contain all the components in one bottle, some components become easily separated; therefore these adhesive require the bottle to be thoroughly shaken immediately before use. However, this shows that there is not only a danger of phase separation while applying the all-in-one adhesive to a tooth surface, but also it means defects may remain if phase separation occurs in the bonding resin layer just prior to polymerization. These problems have been solved with CLEARFIL S3 BOND (Fig 23). Using an air-drying method with a high-pressure air stream has established that fewer clinical errors will occur. As CLEARFIL S3 BOND contains fillers and forms a thin bonding layer after the strong air thinning, more aesthetic restorations, especially in anterior teeth, are possible by eliminating the occasional dark bonding layer line that can occur along the marginal areas when a thick adhesive bond layer occurs.

In the latest product, CLEARFIL S3 BOND PLUS (Fig 24), the bonding performance was further improved by introducing new hydrophilic and hydrophobic resin monomers, new catalyst system, fluoride-releasing function and so on.

7. 2-step or 1-step?

There are various choices of adhesive systems; CLEARFIL SE BOND, CLEARFIL LINER BOND F, CLEARFIL PROTECT BOND, CLEARFIL S3 BOND, or CLEARFIL S3 BOND PLUS in Kuraray Noritake Dental Inc.’s adhesive systems. Basically, a proper application of CLEARFIL SE BOND or CLEARFIL LINER BOND F covers almost all clinical needs and provides highly reliable adhesion. As a one-step adhesive, CLEARFIL S3 BOND PLUS also provides the comparable bonding to CLEARFIL SE BOND. Because of the simplified procedures, 1-step adhesive is considered to be more useful particularly in various clinical conditions. Another concern in clinical application of these adhesive materials is the contraction stress of the composite resin. This is still a significant issue which easily causes the separation between the restoration and cavity floor dentin. The incremental filling technique is recommended to prevent the gap formation at the cavity floor. Using a new facility, Optical Coherent Tomography(OCT), provides really important information to improve restoration with adhesives. The real time observation of the restoration procedures is possible with the OCT without any invasive approach. The restoration including the cavity floor dentin is possible and the gap created at the cavity floor and margins are clearly observed

According to this new analysis, the gap is confirmed to be easily created with most of the adhesives, however, CLEARFIL SE BOND provided the best results in preventing gaps, when the bulk filling was applied to the Class I cavities (4mm in diameter X 2mm in depth) (Fig 25,26). One step adhesives tended to show more gap formation at the cavity floor dentin (Fig 27). Strong bonding during the filling and stress bearing function of bonding resin are considered to be very important to prevent gap formation. Interestingly, gap is propagated during the light irrigation under the real time observation with the OCT. From the consideration above, the CLEARFIL SE BOND is preferable for clinical use.

In the case of the one step adhesives, application of the thin flowable composite lining was confirmed to prevent the gap at the cavity floor and walls. As the use of the flowable composite resin is becoming more common, the one step adhesive, such as CLEARFIL S3 BOND PLUS is also believed to be very practical and reliable in the clinical application.

8. Beyond CLEARFIL SE BOND

CLEARFIL S3 BOND is highly evaluated and widely used internationally because of its recognised adhesive ability. Especially, for its adhesion to dentin, it is considered as gold standard in academic and dental associations concerned with adhesive dentistry. It is also widely accepted in clinical situations. However, enamel bonding is sometimes of concern to clinicians because a frothy surface cannot be obtained after the self-etching primer application. This is true because the surface is already wet with the adhesive resin monomer and other resin monomers. Even when the surface does not look like the phosphoric acid etched enamel, the smear layer is dissolved and the surface is etched creating the irregularity based on the enamel prisms but not based on the enamel prisms. Actually, a strong interfacial bond can be formed (Fig 28-21) to the enamel after mild etching with sophisticated adhesive resin monomers, like MDP. CLEARFIL SE BOND has gained a high reputation amongst clinicians throughout Japan over the past 10 years so much so that the spread and use of total etching with phosphoric acid has virtually become a treatment method of the past. CLEARFIL SE BOND was created by concentrating and connecting very important techniques of adhesive resins, including the history of adhesive resin material development. To students and researchers, who will one day become leaders in their respective fields, understanding and knowing the developmental steps that led to the creation of “CLEARFIL SE BOND” is an excellent means to learn about the inception of present day dental adhesion. It is believed that CLEARFIL LINER BOND F is even more superior to our present day CLEARFIL SE BOND. I would like to close by expressing my deepest appreciation and respect to all of the people who were concerned with the development and success of CLEARFIL products and to the predecessors who contributed to the development of adhesive dentistry which is such an important part of present-day patient care.


References


