Go for Gold!

CLEARFIL™ SE BOND – the 10th Anniversary

The Gold Standard in Dental Bonding
In Recognition of the 10th Anniversary of CLEARFIL™ SE BOND
Junji Tagami DDS, PhD

SPECIAL CONTRIBUTION
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Junji Tagami DDS, PhD:
Professor and Chair, Cariology and Operative Dentistry, Department of Restorative Sciences, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University, Japan

Naoko Seki DDS:
Cariology and Operative Dentistry, Department of Restorative Sciences, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University, Japan

Michael F. Burrow DDS, PhD, MD:
Professor in Restorative Dentistry and Clinical Dean, Melbourne Dental School, The University of Melbourne, Australia

1 Introduction

Over fifty years have passed since Michael Buonocore reported in 1955 that resin adhesion could be improved with phosphoric acid etching of enamel. Since then, adhesive resin technology has changed significantly. Adhesive resin restorations and dental implants have made enormous strides in the second half of the 20th century. Many of the basic principles for restorative techniques have been changed to Minimal Intervention Dentistry, which is a minimally invasive operative approach for treatment of cavitated lesions or healing non-cavitated lesions. Adhesive materials have allowed this philosophical change to be realized.

Kuraray Co., Ltd. (Kuraray Medical Inc., Japan) has played a major role in adhesive resin material development and it is not too much 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 of whom helped to pave the way towards present-day adhesive dentistry.

2 Adhesive Resin Development and Transition

1. Phosphoric Acid Total Etching

(Etch and rinse adhesive systems)

The history of the development of adhesive resin composite as a restorative material started in 1978 with the introduction of CLEARFIL™ BOND SYSTEM-F by Kuraray Medical Inc. (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. Pheny-P (Fig 2) was used as the adhesive resin monomer.

Adhesion to dentin by phosphoric acid etching had not been recognized for a long time. It was only after the 1990’s that the acid etch technique became well known and accepted even in western countries. Later, MDP (10-methacryloyloxydecyl dihydrogen phosphate) was developed as a replacement for Phenyl-P (2-methacryloyloxyethyl phenyl phosphoric acid), and CLEARFIL™ NEW BOND was created (Fig 3).

2. 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 understand adhesive mechanisms to teeth. Primers which are important for promoting good dentin adhesion were invented and introduced, and under the guidance of Prof. Hiroyasu Hosoda and his group led to 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 the etching agent to reduce the damage that occurs from phosphoric acid etching to dentin collagen fibrils. In addition, a primer was also introduced for this adhesive system to dynamically improve adhesion to dentin. One very important research finding was that, after washing and drying etched dentin, the surface collagen fibre network shrank and affected the infiltration of bonding resin. But when a primer was used, it moistened and helped reopen the collagen fibre network and promoted the infiltration of resin. This resulted in a remarkable increase in bond strength (Fig 7). This system also contained CLEARFIL™ LINER BOND PROTECT LINER F, a low viscosity resin composite, similar to a flowable composite resin. Applying this low viscosity resin composite after the bonding procedure also improved adhesion. 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 between the cavity surface and resin restoration.

3. Self-etching Primer Development
Adhesive resin monomers, such as Pheny1-P, MDP, or 4-META (4-methacryloyloxyethyl trimellitic acid anhydride) (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 good adhesion to tooth substrates when using these resin-based adhesives. With the great efforts of corporate R&D, an epoch-making technique of the “self-etching primer” was introduced to the dental profession in 1993. The very first products using this method were CLEARFIL™ LINER BOND 2, adhesive (Fig 8) and, PANAVIA™ 21, resin luting cement, developed by Kuraray Co., Ltd. On account of the improved dentin bond strength of most of the adhesives in the 1990’s, conventional bond test methods could not precisely evaluate adhesive strengths. As a result, a new testing method, the micro tensile bond test, was developed6,7 which enabled bond strength evaluation to become much more accurate by minimizing the adherent areas. The effects of bonding to all parts of normal and caries-affected dentin could now be investigated. The next development of self-etching systems was the introduction of CLEARFIL™ LINER BOND 2V (Fig 9), in which the self-etching primer components were changed and polymerization improved. In 1999, CLEARFIL™ SE BOND (Fig 10), consisting of a one-bottle self-etching primer and one-bottle light-cured bonding agent was invented. In Japan, self-etching primers now have more than 15-years of clinical history. Apprehensiveness towards potentially deficient enamel etching has all but been solved. However, the self-etching primer has shown to be clinically reliable. For those cases of uncut enamel or fluorosed enamel, a short 5 second application of phosphoric acid is possible.

Table 1. The self-etching primer contains MDP, which is the active acidic monomer for demineralizing the enamel and dentin. In addition, the self-etching primer solution contains HEMA as a hydrophilic resin, a dimethacrylate and dentin. In addition, the self-etching primer solution contains HEMA as a hydrophilic resin, a dimethacrylate, catalyst, and some water to permit ionization of the acidic monomers. Its pH is 2.0, which allows simultaneous etching of dentin and enamel without a necessary washing step. After drying with a gentle air stream to remove excess primer, the filled bonding resin is applied and light-cured. The components of the bonding resin are similar to the primer, but do not contain water. The bond has a much greater amount of hydrophobic resin and fillers to ensure a good bond to the resin composite filling material. The invention of the self-etching primer and the establishment of excellent adhesion to dentin by CLEARFIL™ SE BOND brought about advanced research into the adhesive mechanisms to dentin. This led to much more information about hybridized dentin formation and its mechanisms as well as the insight that the use of a self-etching primer and bonding to collagen could be obtained without the water-spray step. Other research showed that to prevent collagen network shrinkage in order to form an adequate bond, even when treated with phosphoric acid etching, it was important to keep the dentin wet. Under these circumstances, wet bonding and moist bonding techniques were proposed6). With those techniques, phosphoric acid etching to dentin was finally recognized in western countries. However, it was obvious that redundant water remaining on the dentin surface inhibited effective bonding. Discussions went on about how much water is necessary to ensure a good bond with wet bonding. However, in Japan, self-etching primer systems had already widely spread into clinical practice, and the wet bonding technique has rarely been 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 the tooth surface during dental cutting procedures. Regions produced after acid treatment, in other words, demineralized areas, even if only slightly, must be hardened and protected by bonding resin infiltration. If not, the areas devoid of resin at the adhesive interface will affect the long-term durability of the bond.

The components of CLEARFIL™ SE BOND are shown in Table 1. The self-etching primer contains MDP, which is the active acidic monomer for demineralizing the enamel and dentin. In addition, the self-etching primer solution contains HEMA as a hydrophilic resin, a dimethacrylate resin, a catalyst, and some water to permit ionization of the acidic monomers. Its pH is 2.0, which allows simultaneous etching of dentin and enamel without a necessary washing step. After drying with a gentle air stream to remove excess primer, the filled bonding resin is applied and light-cured. The components of the bonding resin are similar to the primer, but do not contain water. The bond has a much greater amount of hydrophobic resin and fillers to ensure a good bond to the resin composite filling material. The invention of the self-etching primer and the establishment of excellent adhesion to dentin by CLEARFIL™ SE BOND brought about advanced research into the adhesive mechanisms to dentin. This led to much more information about hybridized dentin formation and its mechanisms as well as the insight that the use of a self-etching primer and bonding to collagen could be obtained without the water-spray step. Other research showed that to prevent collagen network shrinkage in order to form an adequate bond, even when treated with phosphoric acid etching, it was important to keep the dentin wet. Under these circumstances, wet bonding and moist bonding techniques were proposed6). With those techniques, phosphoric acid etching to dentin was finally recognized in western countries. However, it was obvious that redundant water remaining on the dentin surface inhibited effective bonding. Discussions went on about how much water is necessary to ensure a good bond with wet bonding. However, in Japan, self-etching primer systems had already widely spread into clinical practice, and the wet bonding technique has rarely been 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 the tooth surface during dental cutting procedures. Regions produced after acid treatment, in other words, demineralized areas, even if only slightly, must be hardened and protected by bonding resin infiltration. If not, the areas devoid of resin at the adhesive interface will affect the long-term durability of the bond.
The investigation of small voids and defects at the dentin adhesive interface can evaluate the quality of bonding systems used. Silver particles from a silver nitrate solution can infiltrate into the dentin adhesive interface to reveal these subtle voids. The results for CLEARFIL™ SE BOND, using this above method, showed no silver particles at the adhesive interface. This result showed that the method, showed no silver particles at the adhesive interface as shown in Figure 11. This result showed that CLEARFIL™ SE BOND was able to achieve consecutive infiltration and polymerization of resin into tooth substances. Figure 12 shows the adhesive interface between bonding resin and dentin treated with phosphoric acid etching. After phosphoric acid etching, the wet bonding technique was used. Observation of this adhesive interface showed that 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 in 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 that this residual water from wet bonding might have the same effect in the hybrid layer.

Silver particles were observed at the bottom of the hybrid layer, which shows that bonding resin infiltration was insufficient in this area even though collagen fibrils were exposed by phosphoric-acid-etching demineralization. Water as well as silver nitrate can also easily penetrate into this area. Substances which damage the collagen are also able to penetrate. Under 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 durability of adhesion to dentin over the long-term. 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 13). On the other hand, CLEARFIL™ SE BOND does not create such structural defects. Successive interfacial structures have been formed from resin composite, bonding resin, hybrid layer to dentin where etching effects do not reach (Fig 14).

CLEARFIL™ PROTECT BOND (Fig 15) was developed as an adhesive with the same adhesive ability as CLEARFIL™ SE BOND, but it has an antibacterial effect in the primer and also a fluoride-releasing filler in the bonding resin. With the addition of these beneficial effects, adhesive resins are able to not only work as bonding agents, but also as restorative materials to support the prevention of secondary caries. Eighty years of clinical evidence have demonstrated the clinical durability of CLEARFIL™ SE BOND adhesion. There are several other clinical trials of shorter duration which have also demonstrated its clinical success. A time-dependent decrease in dentin adhesion has been reported for all adhesive systems. Though the decrease was subtle compared with an etch and rinse system using phosphoric acid, CLEARFIL™ SE BOND is no exception. However, improvements in adhesive durability were expected for CLEARFIL™ PROTECT BOND due to its fluoride-releasing effect. Indeed, its long-term adhesive durability has greatly improved (Fig 16). In addition, analyses of the adhesive interface structure between dentin and resin revealed that acid- and base-resistant zones exist in the bonded dentin directly beneath the adhesive interface. This is referred to as the acid-based resistant zone. This zone is an area superior to original dentin properties and has been called “Super Dentin”.

It is anticipated that this modification to the dentin will eventually become a new approach in prevention and protection against carious damage of tooth structure. At present, there is a continuing research on the mechanism, however, it is known that the thickness and properties of Super Dentin layers do differ depending on the bonding system used (Fig 18, 19). Among current bonding agents, CLEARFIL™ PROTECT BOND creates the thickest and largest inorganic component rich Super Dentin even after the influence of acid and base. 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. 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 for a longer time. 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.
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5 Characteristics of All-in-one Systems and Bonding

With the increased spread of self-etching techniques and materials, current developments into 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. However, it is also known that the presence of water is not good for the bonding resin layer. To circumvent this contradiction, the air-drying method after the self-etching function of the all-in-one system should be done carefully and prior to light-curing. This step tends to be specific to each product.

Generally, the composition needs a cocktail of resins specific to each product. To maintain this combination of resin monomers in a fluid state, a solvent (acetone, ethanol, etc) must be added in addition to the water to maintain a low pH and the polymerization catalyst system (Table 2).

However, as all-in-one adhesives combine all components in one bottle, some components become easily separated. Therefore these adhesives 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 it also means that defects may remain if phase separation occurs in the bonding resin layer just prior to polymerization. These problems have been solved in CLEARFIL™ S’BOND (Fig 20), and the air-drying method, which uses a high-pressure air stream leading to fewer clinical errors to occur.

As CLEARFIL™ S’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.

1. Provide a clean surface before and during bonding procedures.
2. Place a sufficient amount of self-etching primer or all-in-one type, CLEARFIL™ S’BOND on the tooth surface. Do not shorten application time.
3. Dry the newly treated surface with high-pressure air blow after applying the self-etching primer or CLEARFIL™ S’BOND.
4. Light-cure the bonding sufficiently.

Concerning light irradiation and bonding, adhesive is of dual-cured type. So, try to light-cure for as long as circumstances allow. Light intensity decreases as the distance from the light-cure tip to the treated surface increases, and adhesive strength also decreases (Fig 22, 23)\(^1\). Extending light irradiation time or using high-power light-curing units is recommended. CLEARFIL™ SE BOND can now be regarded as an adhesive standard. But, as an example of choosing an adhesive system depending on each clinical case, CLEARFIL™ S’BOND can be recommended for anterior teeth restorations where the margin is located on the labial surface.

That is because of its feature of a thin bonding layer. However, with a proper bevel, CLEARFIL™ S’BOND does not create dark bonding layer lines either. Some pointed out a slight decrease in adhesive strength by making the CLEARFIL™ SE BOND bonding layer thinner, but clinically, it is not considered as a significant decrease, so CLEARFIL™ SE BOND can be used with moderately high pressure air blow to make the bond layer thinner. CLEARFIL™ DC BOND is designed for direct resin composite core build-up. It is a dual-cured type used on the assumption that sufficient polymerization will not be possible at the bottom of a post even with light irradiation. CLEARFIL™ DC BOND is a one-step type, self-etching bonding agent with the same techniques used in the development of CLEARFIL™ S’BOND, but since chemical polymerization (auto polymerization) character is added, it consists of two bottles. To obtain maximum adhesion, mix the two liquids together immediately before use because of the volatility of the ethanol solvent. Dry the entire treated surface sufficiently using air since the adhesive contains water. Light-cure sufficiently as the pulp floor and chamber and post tip are parts where light irradiation deficiency occurs early. CLEARFIL™ PROTECT BOND, as mentioned above, is expected to increase as it is a superior adhesive system to CLEARFIL™ SE BOND, and it should be a standard product for adhesion in the future.

Currently, with its anti-bacterial and fluoride-releasing effects, CLEARFIL™ PROTECT BOND is recommended for patients and areas that exhibit high caries risk, cavities with large dentin margins, or cases of suspicious caries dentin inner layer (lesions where bacteria left in situ) remaining.

Table 2

<table>
<thead>
<tr>
<th>Basic compositions of one-step adhesives.</th>
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<tbody>
<tr>
<td>• adhesive resin monomer (MFP-4-META, MA10, etc)</td>
</tr>
<tr>
<td>• hydrophilic monomer (HEMA, etc)</td>
</tr>
<tr>
<td>• hydrophilic monomer ( Bis-GMA, UDMA, etc)</td>
</tr>
<tr>
<td>• solvent (acetonitrile, ethanol, etc)</td>
</tr>
<tr>
<td>• water</td>
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<tr>
<td>• catalyst</td>
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6 Variations of CLEARFIL™ Bonding Systems

There are various choices of adhesive systems: CLEARFIL™ SE BOND, CLEARFIL™ PROTECT BOND, CLEARFIL™ S’BOND or CLEARFIL™ DC BOND (Fig 21) in Kuraray Medical Inc.’s adhesive systems. Basically, a proper application of CLEARFIL™ S’BOND covers almost all clinical needs and provides highly reliable adhesion. Here are some basic points to be reviewed to achieve maximum adhesive ability of Kuraray Medical Inc.’s adhesive systems.
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CLEARFIL™ SE BOND is highly evaluated and used internationally because of its recognised adhesive ability. Especially for its adhesion to dentin, it is considered as a gold standard in academic and dental associations concerned with adhesive dentistry. It is also widely accepted clinically. However, 3-step etch and rinse adhesive systems are still considered by some western researchers to be among the best adhesives. A strong interfacial bond can be formed (Fig 24-27) to the enamel after mild etching with the sophisticated adhesive resin monomers, like MDP, but this is still not recognized, possibly because the self etching materials do not exhibit the typical etching pattern of enamel prisms that is formed after phosphoric acid etching. Perhaps it is up to university researchers and clinicians to reflect on this matter, and work to improve our knowledge and evidence base to show the clinical advantages of the self-etch system philosophy.

CLEARFIL™ SE BOND has gained an excellent 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. Many of our current concepts and ideals of adhesive dentistry gained their initial introduction in Japan from the work by Professors Fusayama and Masuhara. In this field, Kuraray Medical Inc. has also played an extremely important and active role to create CLEARFIL™ SE BOND, one of the world’s top bonding agents, and the introduction of the self-etching adhesive system concept.

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. CLEARFIL™ SE BOND forms an excellent basis for future versions of adhesive resin material which might become even superior to our present day CLEARFIL™ SE BOND.

References
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Your Contact
Kuraray Europe GmbH
BU Medical Products
Hoechst Industrial Park/F 821
65926 Frankfurt am Main
Germany

Telephone: +49-(0)69-305 35825
Fax: +49-(0)69-305 98 35825
E-mail: dental@kuraray.eu
Website: www.kuraray-dental.eu