

The concept of super enamel formation —Relationship between chemical interaction and enamel acid-base resistant zone at the self-etch adhesive/enamel interface

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Self-etch adhesive (SEA) systems simplify bonding procedures. It is believed that good mechanical retention and chemical bonding are both important factors to obtain reliable bonding to enamel. The enamel acid-base resistant zone (ABRZ) has been confirmed at the adhesive/enamel interface by scanning electron microscopic observation. However, the formation of enamel ABRZ is influenced by the type and components of adhesive systems. Chemical interactions by a functional monomer with hydroxyapatite strongly support the explanation of the mechanism for enamel ABRZ formation. The ABRZ created by MDP-containing SEA systems has shown good potential to resist acid attack from simulated recurrent caries models. In addition, fluoride release may enhance acid resistance. It has been proposed that such a reinforced enamel be termed “Super Enamel”. The concept of the formation of super enamel may contribute to protecting enamel, and conserve tooth structure leading to improved restoration longevity.

Keywords: Acid-base resistant zone, MDP, Self-etch adhesive, Super enamel

INTRODUCTION

Enamel is characterized by a complex three-dimensional relationship of prisms and interprismatic structures, which predominantly consist of an inorganic matrix of carbonated hydroxyapatite (HAp) crystals with a small quantity of organic constituents (*i.e.* proteins and lipids) and water occupying the gaps between the apatite crystals¹.

Since the development of dental-adhesive techniques and concepts in the 1950's, phosphoric acid has been employed as the standard agent to etch the enamel prior to application of a resin-based adhesive². Phosphoric acid etching modifies the enamel surface topography, substantially increasing its surface energy to the direct benefit of enhancing its wettability³. In general, the extent and depth of the etching pattern produced by phosphoric acid, which provides the micro-mechanical interlock, primarily determines the bonding receptiveness of enamel. Variation in regional enamel and prism orientation of the tooth crown is known to influence the bonding performance of resin-based adhesives⁴.

Nowadays, it is believed that good mechanical retention and chemical bonding are both important factors to obtain reliable bonding to enamel based on chemical and morphological studies.

ADVANTAGE OF SELF-ETCH ADHESIVE (SEA) SYSTEMS

A two-step self-etch adhesive (2-SEA) system, Clearfil Liner Bond II (Kuraray Medical, Tokyo, Japan) was first introduced to the profession in 1993. This was the

first true self-etching priming system being comprised of a self-etching primer and an adhesive resin. In SEA systems, an acidic functional monomer plays an important role acting as the etching agent for the enamel, thus allowing resin monomers to penetrate into the demineralized enamel, and chemically interact with HAp crystals⁵⁻⁸. One of the analogues of phosphoric acid-based monomers, 10-methacryloyloxydecyl dihydrogen phosphate (MDP, Fig. 1) has been widely accepted as a functional monomer in SEA systems⁹. Indeed, SEA systems containing MDP have shown consistent adhesive performance in numerous laboratory and clinical studies, particularly regarding long-term bond durability^{10,11}.

CHEMICAL INTERACTION OF MDP TO HAP

Yoshida and others^{8,12} measured the chemical propensity of functional monomers, such as MDP, 2-methacryloyloxyethyl phenyl hydrogen phosphate (Phenyl-P, Fig. 1) and 4-methacryloxyethyl trimellitic acid (4-MET) to HAp. They demonstrated that the chemical propensity of MDP to interact with HAp was the highest, followed by 4-MET and Phenyl-P. MDP created a strong and stable MDP-Ca salt, which contributes to strong and stable bonding to mineralized tooth tissue, while Phenyl-P only showed a weak chemical interaction with HAp. Bista *et al.*⁵ confirmed the chemical adsorption of MDP onto the HAp surface under neutral conditions by employing the Langmuir isotherm model. The principal adhesion mechanism of MDP-based 2-SEA can be explained by the intermediary layer formation on the MDP ionically bonding to the calcium of HAp in enamel and dentin⁶. Yoshihara *et al.*¹³ reported a double

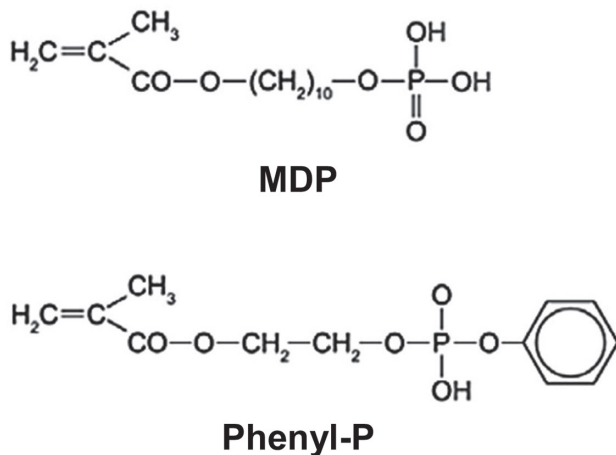


Fig. 1 Chemical formulae of MDP and Phenyl-P. MDP; 10-methacryloyloxydecyl dihydrogen phosphate, Phenyl-P; 2-methacryloyloxyethyl phenyl hydrogen phosphate

membrane structure with MDP created at the adhesion front of the adhesive-dentin interface in the 2-SEA system, Clearfil SE Bond (Kuraray Noritake Dental, Tokyo, Japan). The double membrane structure consists of two MDP molecules with their methacrylate groups directed toward each other and their phosphate groups directed away from each other with calcium salts being deposited between the layers of the phosphate groups¹³.

However, the stability of MDP in SEA may be different between 2-SEA and 1-step-SEA systems (1-SEA)¹⁴. Fujita *et al.*^{6,15} analyzed the types of molecular species of MDP-Ca salts and the quantities produced during a 1-min application of MDP-based all-in-one adhesives (1-SEA) to enamel and dentin using nuclear magnetic resonance (NMR) techniques. From the curve-fitting analysis of the ³¹P NMR spectra of enamel and dentin reactant residues, the following four types of MDP-Ca salts were elucidated; a mono-calcium salt of the MDP monomer (MCS-MM), di-calcium salt of the MDP dimer (DCS-MD), MCS-MD and DCS-MM were assigned, while a double membrane structure was observed in the 2-SEA system. This double membrane was not detected in 1-SEA adhesive systems even in those systems that contained MDP functional monomer^{6,15}.

ULTRASTRUCTURAL EXAMINATION OF THE DENTIN-ADHESIVE INTERFACE

Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) examinations of the bonded interface have given useful information to better understand the bonding mechanisms of adhesives to tooth substrates. For dentin bonding, the hybridization theory has been widely accepted, in which a resin monomer penetrates into demineralized dentin and polymerizes *in situ*, resulting in formation of a hybrid layer, which is an intermingling of resin with the collagen fibres of

the dentin¹⁶.

Tsuchiya *et al.*¹⁷ reported an acid-base resistant zone (ABRZ) beneath the hybrid layer of a SEA-dentin interface after an acid then base challenge. Inoue *et al.*¹⁸ standardized the specimen preparations for both SEM and TEM examinations, which were able to clearly visualize the formation of the ABRZ at the adhesive-dentin interface. The ABRZ is believed to play an important role in inhibiting damage from recurrent caries by sealing restoration margins which can then promote restoration durability by maintaining the bond¹⁹. However, ABRZ formation has been shown to be adhesive material dependent, where it has been identified in SEA systems, but not in etch and rinse adhesive systems^{20,21}. It remains poorly understood how the mechanism of dentin ABRZ forms. It thought it is probably due to a complex interaction of dentin structures which includes both the inorganic and organic components of the dentin^{19,22}.

ENAMEL ABRZ AT ADHESIVE-ENAMEL INTERFACE

Li *et al.*²³ used SEM to evaluate the effect of functional monomers such as MDP and Phenyl-P as shown in Fig. 1, with regard to the morphology of an enamel ABRZ. They used two experimental self-etching primers and two adhesive agents including either MDP or Phenyl-P, meaning a total of four different combinations of 2-SEA systems were used. As described above, MDP and Phenyl-P are analogous phosphoric acid monomers, showing very different characteristics in their chemical propensity to interact with HAp (MDP»Phenyl-P). The evaluation also looked at the morphological differences of the adhesive-enamel interfaces after acid-base challenge among the four adhesive systems. It was concluded that an enamel ABRZ was observed in those SEAs containing MDP in either both or one component of the self-etching primer and the bonding agent (Fig. 2A). However, no enamel ABRZ was created in the combination of the Phenyl-P containing primer and the Phenyl-P-containing bonding agent (Fig. 2B). These morphological differences in enamel ABRZ between MDP and Phenyl-P-containing SEA systems confirm the evidence of the chemical propensity of the functional monomers of MDP and Phenyl-P to interact with HAp. Hence, it seems that MDP in either a self-etching primer or an adhesive is able to react with the enamel surface to create a stable MDP-Ca salt at the adhesive interface. On the other hand, Phenyl-P seems unable to create a stable chemically linked interface that can resist acid attack because of a lack of a Phenyl-P-Ca salt. When the bonded specimen of the Phenyl-P-containing adhesive system was subjected to acid attack, the adhesive-enamel interface was more easily dissolved than the intact enamel. This resulted in the erosion of the enamel at the adhesive-enamel interface. These phenomena demonstrate that selection of a suitable functional monomer is essential to achieve stable enamel bonding in 2-SEA systems. The calcium salt of MDP is the key to create a stable enamel ABRZ.

Fujita *et al.*⁶ suggested that the calcium salt

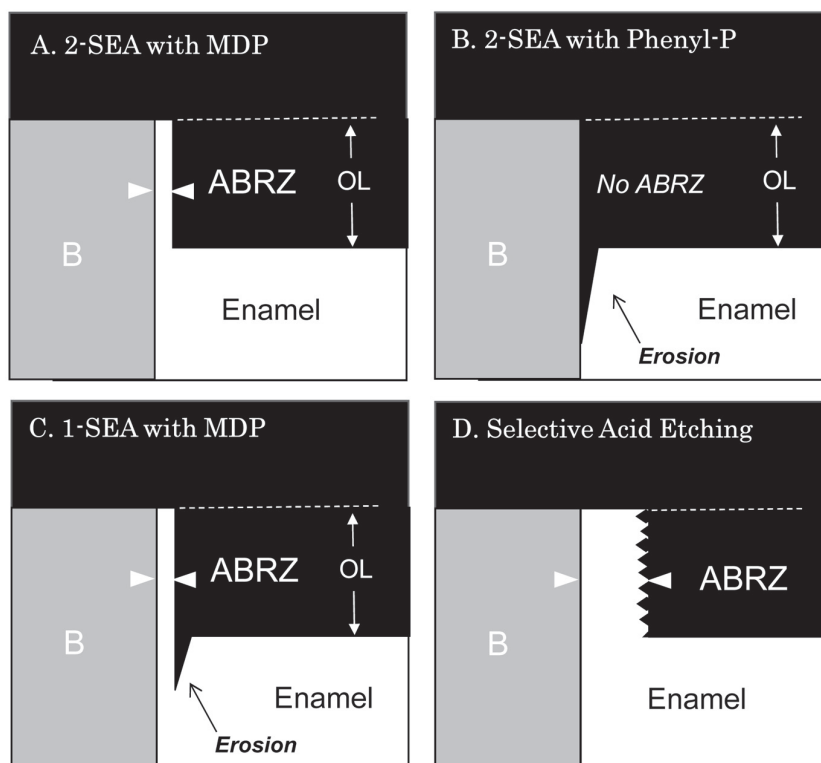


Fig. 2 Illustrations to explain morphological differences in enamel ABRZ. A: 2-SEA system containing MDP; enamel ABRZ is clearly created at the adhesive/enamel interface. B: 2-SEA system containing Phenyl-P; no enamel ABRZ is created at the adhesive/enamel interface. Erosion is created along the interface (arrow). C: 1-SEA system containing MDP; enamel ABRZ is created at the adhesive/enamel interface, however, erosion is created beneath the enamel ABRZ (arrow). D: Selective acid etching prior application of a SEA system; thick enamel ABRZ is create at the adhesive/enamel interface. No erosion is detected at the interface.

formation with MDP would decrease the ability to polymerize the vinyl group of MDP because of limited mobility of the MDP molecule during polymerization which would cause a decrease in the polymerization conversion of the bonding resin at the adhesive/enamel interface. If so, polymerization of MDP monomer may not be essential to create an enamel ABRZ. Further study is needed to analyze the behavior of the MDP monomer and how it participates in the calcium salt formation after polymerization of an MDP-containing adhesive.

SELECTIVE ENAMEL ETCHING PRIOR TO 1-SEA

1-SEA systems, the so-called all-in-one adhesives, combine etching, priming and bonding into one procedure. The 1-SEAs contain acidic functional monomers, hydrophilic and hydrophobic monomers, water and organic solvents in a single solution²⁴. Recently, the multimode concept has been introduced, where some 1-SEAs can be used either in self-etching mode, selective-etch mode, or etch-and-rinse mode^{7,25}.

Sato *et al.*²⁶ evaluated the formation of ABRZ at enamel interfaces with 1-SEA systems. They reported that 2-SEAs containing MDP created a stable enamel

ABRZ, whereas the 1-SEAs containing MDP or MDP analogues created thinner ABRZs with a funnel-shaped erosion, indicating a weak area that is vulnerable to acid-base attack beneath the adhesive-enamel interface (Fig. 2C)²⁶. Hydrophilic ingredients and/or organic solvents in 1-SEAs may interfere with the stable bond at the enamel interface which is less resistant to acid attack. Fujita *et al.*⁶ reported that HEMA contained in a 1-SEA reduced MDP-Ca salt formation. The MDP-based HEMA-containing 1-SEA showed a slower production rate of MDP-Ca salt than HEMA-free 1-SEA. The observed delay in the production rate of the MDP-Ca salt was believed to be due to HEMA controlling ionization of the phosphate group in MDP, since MDP is dissolved in HEMA more preferentially than the water that is included in these systems to maintain the acidity.

Selective enamel etching has been considered as a strategy for optimizing enamel bond strength of self-etch and the so-called universal adhesives²⁷. From the results of a previous study, selective phosphoric acid etching is necessary prior to application of 1-SEAs²⁸. Phosphoric acid etching prior to 1-SEA application led to the formation of a thicker ABRZ and no funnel-shaped erosion occurred at the adhesive-enamel interface when

it was exposed to the acid-base challenge (Fig. 2D)²⁶. Sato *et al.*⁷ suggested that the penetration of resin monomers into the etched enamel surface may have encapsulated its crystallite components to provide an effective seal and protect the outermost enamel from dissolution from an acid attack.

FLUORIDE RELEASE AND BLEACHING ENAMEL

Previous studies suggested that the fluoride-containing adhesives had a positive effect on the stability of the ABRZ^{29–33}. The bonding agent of Clearfil Protect Bond (Kuraray Noritake Dental) contains surface-treated sodium fluoride (NaF) crystals which are able to release fluoride ions from the adhesive²⁹. Kakiuchi *et al.*³⁴ reported that addition of both MDP and NaF into the adhesive improved the microshear bond strength of the 2-SEA system to enamel and also enhanced the acid resistance of the adhesive-enamel interface. Bista *et al.*⁵ reported that the presence of NaF as an ingredient in the adhesive improved the adsorption of neutralized MDP to the HAp surface, suggesting additional benefits for reinforcing the adsorption of MDP and inhibiting demineralization.

Nanoleakage has been described as leakage within nanometer-sized channels along an adhesive interface^{14,35,36}. In the case of enamel, nanoleakage may be caused by insufficient infiltration of resin into the demineralized enamel or by incomplete polymerization of hydrophilic monomers in the nanometer-sized interfacial spaces. Halabi *et al.*³⁷ reported that nanoleakage was observed along the enamel prismatic planes in a 1-SEA (G-Premio Bond, GC, Tokyo, Japan), in which the silver deposits were scattered in the superficial enamel up to a depth of approximately 50 μm from the interface. However, nanoleakage was not observed in in-office-bleached specimens. In addition, application of the bleaching agent created a thick (about 1 to 2 μm) ABRZ. Generally, the mechanism of action of bleaching enamel is related to hydrogen peroxide as a strong oxidizing agent. The oxidation from the bleaching agent is able to denature proteins which increases tissue permeability and hence allows the movement of ions through the enamel more easily, while the residual oxygen from the bleaching agent interferes with resin polymerization^{38,39}. Bleaching enamel contributed to prevention of nanoleakage at the interface and formation of a thick ABRZ. It is believed this may be due to an increase in enamel porosity after bleaching, leading to deeper penetration of the 1-SEA which seems to result in an improved chemical interaction of the monomer with HAp.

CONCEPT OF THE FORMATION OF SUPER ENAMEL

The ABRZ created by an MDP-containing SEA system has a good potential to resist the acid attack from recurrent caries. In addition, fluoride release from SEA may enhance the acid resistance. Chemical bonding of

MDP to enamel is necessary to form a stable enamel ABRZ, which is supported by the research outcomes showing a stable MDP-Ca salt can be formed⁸. A hybrid layer is created at the adhesive/dentin interface, which is defined as monomer penetration and polymerization around the collagen fiber network¹⁶. However, a hybrid layer based on its original definition is not created at an adhesive/enamel interface, since enamel does not contain collagen³⁸. Therefore, the mechanism of enamel ABRZ formation must be different from hybridization. Enamel ABRZ formation is believed to be a result of a chemical reaction of a functional monomer with HAp. This is comprised of two processes, namely, the monomer approaches closely to HAp and then a chemical reaction of a functional monomer with the HAp at adhesive/enamel interface takes place. A neutral condition (pH 7) is essential to create stable calcium salts from a functional monomer at the adhesive/enamel interface⁵. Previously, we have proposed the terminology “Super Dentin” at the adhesive/dentin interface based on the phenomenon of dentin ABRZ formation^{22,40}. The dentin ABRZ formation can also be explained by the same mechanisms described above from the interaction of the functional monomer and HAp at the demineralized front beneath the hybrid layer. Therefore, the reinforcement of the etched enamel by the resin interactions and chemical interaction with a functional monomer should therefore be termed “Super Enamel”. The conceptual formation of super enamel may contribute to protecting enamel, and conserve tooth structure for improved restoration longevity.

CONCLUSION

Morphology of an enamel ABRZ is adhesive material dependent. The MDP-containing 2-SEA system is able to create a stable enamel ABRZ, which has good potential to resist an acid attack from a cariogenic biofilm. From the morphological and chemical evidence at adhesive/enamel interface, it is proposed that this resin-reinforced enamel be termed “Super Enamel”. The concept of super enamel formation may contribute to protecting enamel, and conserve tooth structure for improved restoration longevity.

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