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J Dent Res 83(4):290-295, 2004

ABSTRACT

One-step self-etch adhesives behave as permeable membranes after polymerization, permitting water to move through the cured adhesives. We hypothesize that osmotic blistering occurs in bonded enamel when these adhesives are used without composite coupling. Tooth surfaces from extracted human premolars were bonded with 5 one-step self-etch adhesives. They were immersed in distilled water or 4.8 M CaCl₂, and examined by stereomicroscopy, field-emission/environmental SEM, and TEM. Water blisters were observed in bonded enamel but not in bonded dentin when specimens were immersed in water. They collapsed when water was subsequently replaced with CaCl₂. Blisters were absent from enamel in specimens that were immersed in CaCl₂ only. Water trees were identified from adhesive-enamel interfaces. Osmotic blistering in enamel is probably caused by the low water permeability of enamel. This creates an osmotic gradient between the bonded enamel and the external environment, causing water sorption into the interface.

KEY WORDS: osmosis, water blisters, enamel, self-etch, water trees

Osmotic Blistering in Enamel Bonded with One-step Self-etch Adhesives

INTRODUCTION

Contemporary dentin adhesives are available as three-step, two-step, and one-step systems, depending on how the 3 cardinal steps of etching, priming, and bonding to tooth substrates are accomplished (Inoue *et al.*, 2001). For self-etch adhesives, two-step self-etching primers have been simplified into one-step self-etch (all-in-one) adhesives that etch, prime, and bond simultaneously (Perdigão, 2002). All-in-one adhesives are mostly available as two-component assemblies, with the water component separated from the functional acidic monomers to prevent their hydrolysis during storage (Pashley and Tay, 2001). Recently, one manufacturer introduced a one-bottle all-in-one adhesive, and claimed that reliable results can be achieved without the concern for hydrolytic degradation of the ester linkage of 4-methacryloxyethyltrimellitic acid (4-MET) in the adhesive.

Because of the high concentrations of hydrophilic and acidic resin monomers, low film thicknesses, and lack of more hydrophobic coupling resin layers (Cheong *et al.*, 2003), one-step self-etch adhesives have been reported to behave as permeable membranes after polymerization (Tay *et al.*, 2002a). This is due to the presence of water-attracting hydrophilic domains (Zaikov *et al.*, 1988) and water trees (*i.e.*, interconnecting water-filled channels) within the polymerized adhesives (Tay *et al.*, 2002b) that permit water to move from the underlying dentin through the adhesive. Water droplets that collect along the adhesive surface are trapped by the hydrophobic coupling composite as water blisters. Fluid flow through porous films (Zentner *et al.*, 1985) does not occur when completely dehydrated dentin (Tay *et al.*, 2003b) or relatively impermeable substrates such as composites are bonded with these adhesives (Tay *et al.*, 2003a).

Osmotic blistering (Pommersheim and Nguyen, 1998) is a well-recognized problem in the resin paint-coating industry. Classic osmotic blistering occurs in the opposite direction when resin-coated, impermeable substrates are immersed in water (*e.g.*, boat hulls). In the presence of contaminating ions on a substrate surface, osmotic cells are initiated between the coating and substrate (van der Meer-Lerk and Heertjes, 1975). The osmotic gradient causes water to flow from the outside into the interface. Blister formation occurs, since there is no channel for the relief of the osmotic pressure in an impermeable substrate. With time, the blisters enlarge to a point where adjacent blisters coalesce, eventually resulting in the delamination of the resin coating. Blister initiation may be prevented by reversing the concentration gradient, such as when a concentrated salt solution is placed outside the coating, to counterbalance the hypertonicity of the resin-enamel interface. This reversed phenomenon parallels what has been observed along adhesive-dentin interfaces.

Although dentin adhesives are usually coupled to composites when they are applied to dentin, direct exposure of adhesive-coated enamel to the oral environment may occur when these adhesives are used as dentin desensitizers (Prati *et al.*, 2001), as adhesive flash during the bonding of orthodontic

Received March 17, 2003; Last revision February 6, 2004;
Accepted February 9, 2004

brackets (Bishara *et al.*, 2001; Korbmacher *et al.*, 2002), for sealing of ground enamel surfaces (Glasspoole *et al.*, 1999; Kuhar *et al.*, 1999) following interproximal stripping, or with the use of filled self-etch adhesives as alternatives for conventional pit-and-fissure sealants (Simonsen, 2002). Since enamel is less permeable than intertubular dentin (ten Bosch *et al.*, 2000; De Munck *et al.*, 2003), it is anticipated that the classic features of osmotic blistering may occur when enamel coated with a one-step self-etch adhesive is placed in water. Thus, the objective of this study was to test the hypothesis that osmotic blistering occurs when one-step self-etch adhesives are used as enamel coatings in the absence of additional composite coupling.

MATERIALS & METHODS

In vitro Study

Twenty-four non-carious human premolars were collected after the patients' informed consent had been obtained under a protocol reviewed and approved by the institutional review board of the Medical College of Georgia (Augusta, GA, USA). Within one month of extraction, the roots of these teeth were removed along the cemento-enamel junction by means of a slow-speed saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under water-cooling. The crown of each tooth was further sectioned longitudinally into two halves. The exposed tooth surfaces were polished with wet 180-grit silicon carbide paper.

Experimental Design

Five one-step self-etch adhesives were examined in this study. They included 4 two-component systems (Prompt L-Pop and Adper Prompt, 3M ESPE, St. Paul, MN; One-Up Bond F, Tokuyama Corp., Tokyo, Japan; Xeno III, Dentsply DeTrey, Konstanz, Germany) and one single-component system (iBond, Heraeus Kulzer, Hanau, Germany). Four teeth were used for each adhesive. The numbers of coats of adhesives that were applied to the tooth halves and light-cured were in accordance with the manufacturers' instructions.

Optical Microscopy

The bonded tooth surfaces were examined without additional composite coupling. Since it was impossible to differentiate between adhesive-coated enamel and dentin under a scanning electron microscope, we first determined the location of osmotic

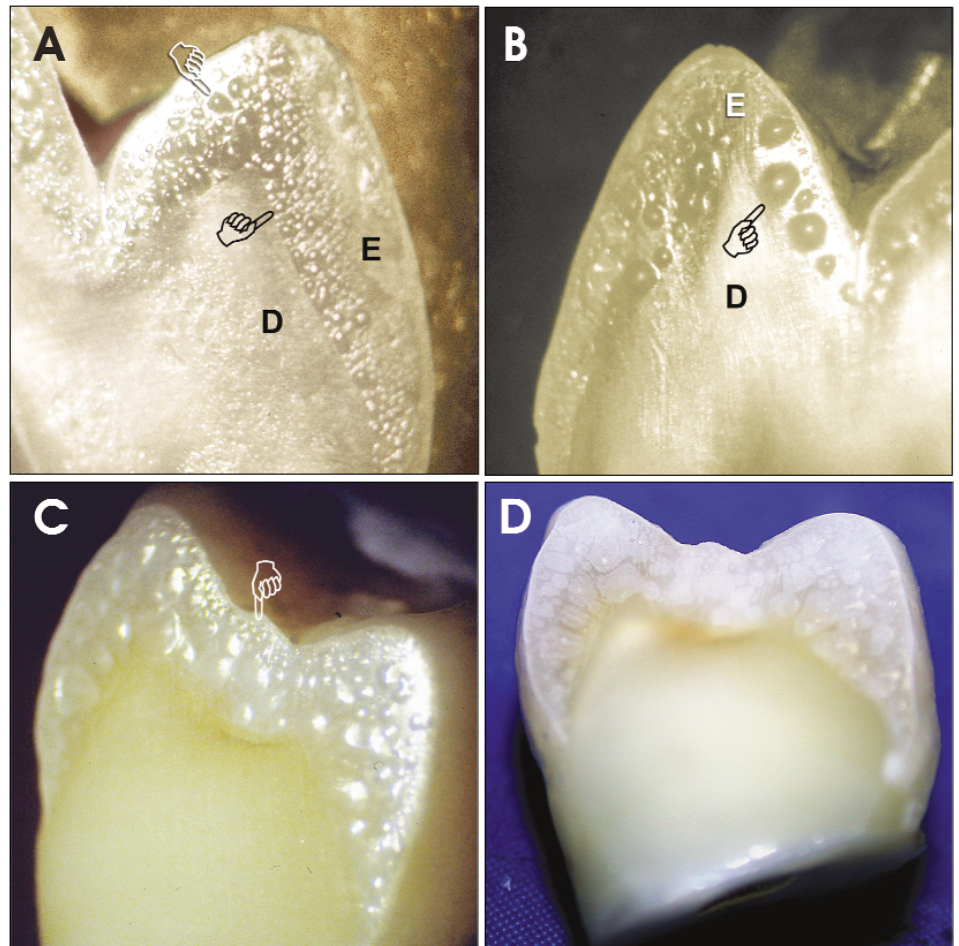


Figure 1. Optical micrographs illustrating the phenomenon of osmotic blistering in enamel. (A,B) Optical microscopy photographs illustrating the phenomenon of osmotic blistering in enamel bonded with one-step self-etch adhesives such as (A) Adper Prompt and (B) iBond. Water blisters (pointers) are present between the adhesive and enamel (E) after the bonded specimen was immersed in water for 30 min. No water blisters can be observed in the bonded dentin (D). (C,D) A series of photographs taken from specimens bonded with One-Up Bond F, showing the effect of reversal of the osmotic gradient on existing water blisters. (C) Water blisters that were formed in enamel (pointer) but not dentin after immersion in distilled water for 30 min. (D) The same specimen after re-immersion in the CaCl_2 solution for 10 min. Collapse of the blisters occurred due to the withdrawal of water from the blisters into the external salt solution.

blistering from one half of each tooth using a stereomicroscope (Nikon SMZ10, Tokyo, Japan) at 20-30X magnification.

For each adhesive, 3 bonded specimens were immersed in distilled water for 30 min before examination. After examination, they were replaced in distilled water for 30 min, followed by immersion in 4.8 M CaCl_2 for 10 min to reverse the osmotic gradient. The last specimen was immersed for 30 min in the CaCl_2 solution only, without prior immersion in distilled water, and was used as a control.

Field Emission-Environmental Scanning Electron Microscopy (FE-ESEM)

The other half of each tooth was bonded similarly when it was scheduled for FE-ESEM examination, with the same sequence of fluid immersion as described previously. The bonded specimens were examined with a FE-ESEM (Philips XL-30, Eindhoven, The Netherlands) under wet conditions (Cowan *et al.*, 1996).

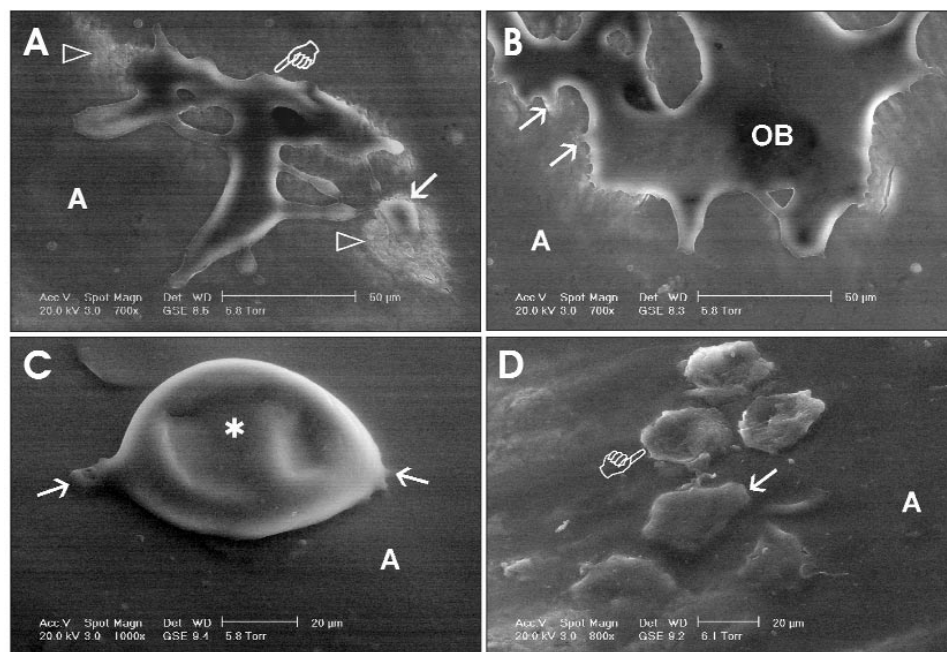


Figure 2. FE-ESEM micrographs demonstrating the appearance of osmotic water blisters after enamel bonded with different one-step self-etch adhesives was immersed in water. (A) A single water blister (arrow) in Adper Prompt that was found next to a large, irregular blister (pointer). The latter were more commonly observed in this adhesive and were probably formed by the coalescence of multiple smaller blisters. The surface texture of the adhesive (A) adjacent to the blisters was also altered (open arrowheads), and appears swollen and exhibits cracking, even when the specimen was examined under wet conditions. (B) Another view of a coalesced osmotic water blister (OB) in Adper Prompt, showing that the film coating that formed the blister wall was derived from, and is still connected with (arrows), the underlying adhesive resin (A). (C) A partially collapsed blister in Xeno-III-bonded enamel after the specimen was re-immersed in the concentrated CaCl_2 solution. The top of the blister (asterisk) is partially collapsed. Connection of blister with the underlying adhesive can be clearly identified (arrows). A, adhesive. (D) Partial (arrow) and complete collapse of the pre-existing water blisters in iBond after re-immersion in the concentrated CaCl_2 solution. Subsurface adhesive cratering (pointer) can be observed beneath the completely collapsed blisters.

Examination was conducted without coating at 15 kV, with the temperature of the Peltier (cooling) stage fixed at 4°C and the vapor pressure of the vacuum chamber varying between 5.8 and 6.3 Torr, to generate a relative humidity of 99-100%.

Transmission Electron Microscopy (TEM)

Prompt L-Pop and iBond were selected for TEM examination. The adhesives were similarly applied to the sectioned tooth halves but were coupled with a microfilled composite (EPIC-TMPT, Parkell, Farmingdale, NY, USA) to prevent osmotic blistering from damaging the resin-enamel interfaces. The bonded interfaces were immersed in a 50 wt% ammoniacal silver nitrate tracer solution for 24 hrs, followed by immersion in a photodeveloping solution to reduce the diamine silver ions into metallic silver grains, according to the nanoleakage protocol described by Tay *et al.* (2002b). Undemineralized, unstained, epoxy-resin-embedded, 90-nm-thick sections were prepared and examined under a TEM (Philips EM208S) operated at 80 kV.

In vivo Study

To validate the clinical fidelity of the *in vitro* results, we applied the adhesives to the labial enamel surfaces of the central incisors of two co-authors, after obtaining their informed consent to a protocol that was reviewed and approved by the institutional review board of the Medical College of Georgia (Augusta, GA, USA). Documentation

was performed by both direct and indirect techniques. For the direct technique, clinical photographs were taken at different periods after the application of the adhesive to labial enamel. High-magnification clinical photographs were also taken with a camera attached to an endodontic microscope (OPMI pico, Carl Zeiss, Oberkochen, Germany). For the indirect technique, polyvinyl siloxane impressions (Affinis LightBody; Coltène AG, Altstätten, Switzerland) were taken of the adhesive-bonded enamel, from which epoxy resin replicas were prepared, according to the replica technique reported by Itthagarun and Tay (2000). The replicas were coated with gold/palladium and examined under a SEM (JEOL, Model 5400, Tokyo, Japan) at 5-10 kV.

RESULTS

When bonded specimens were immersed in distilled water, optical microscopy clearly showed that osmotic blistering occurred in enamel but not in dentin. This phenomenon was seen in all the one-step self-etch adhesives examined and is illustrated with specimens bonded with Adper Prompt (Fig. 1A) and iBond (Fig. 1B). For Prompt L-Pop, osmotic blistering in enamel was so severe that delamination

of the adhesive layer could be seen within 30 min of water immersion. No osmotic blistering could be observed when the bonded specimen was immersed in the control CaCl_2 solution (not shown). The effect of reversing the osmotic gradient on existing water blisters is illustrated by specimens bonded with One-Up Bond F. Osmotic blisters that were located in enamel after 30 min of water immersion (Fig. 1C) were almost completely collapsed after re-immersion in the CaCl_2 solution (Fig. 1D).

ESEM images of osmotic blistering that occurred in Adper Prompt are shown in Fig. 2. Both individual blisters and large irregular blisters that were formed by the coalescence of smaller blisters could be identified (Fig. 2A). Subsurface adhesive damage could be seen around the blisters when these specimens were examined under wet conditions (Fig. 2B).

The effect of reversing the osmotic gradient on pre-existing water blisters could be observed in detail under ESEM examination. In Xeno-III-bonded specimens, individual fully developed water blisters that were seen after immersion in water became partially collapsed following re-immersion in the CaCl_2 solution (Fig. 2C). Similar features were also observed in specimens bonded with iBond, with subsurface cratering occurring beneath the thin, adhesive film derived from the collapsed blisters (Fig. 2D).

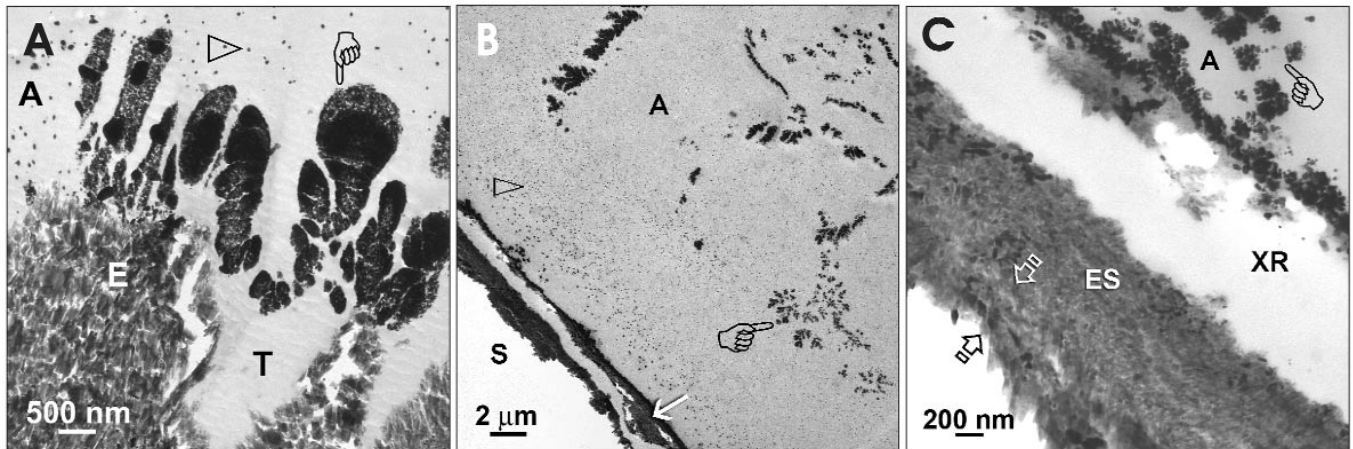


Figure 3. TEM micrographs demonstrating the pathways of water movement through one-step self-etch adhesives. The micrographs were taken from unstained undemineralized sections of adhesive-bonded enamel that were immersed in an ammoniacal silver nitrate tracer solution. Water trees (pointers) can be identified within the adhesives. In addition, isolated silver grains (open arrowheads), probably representing the hydrophilic resin domains, can be observed throughout the adhesive-enamel interfaces. They represent the pathways for water movement within the polymerized adhesives (A). (A) In the more aggressive self-etch adhesive, Prompt L-Pop, the enamel smear layer is completely dissolved, and water trees are seen along the surface of the enamel hybrid layer (R) and above the resin tags (T). (B) In the mild self-etch adhesive iBond, the enamel smear layer (arrow) is incompletely dissolved and separated from the adhesive during specimen preparation. S, empty grid space. (C) A high-magnification view of Fig. 3B, showing the hybridized enamel smear layer (ES) that separated from the adhesive and was probably embedded by the laboratory epoxy resin (XR). The hybridized smear layer consisted of fractured chips of enamel crystallites and can be distinguished from the underlying 300- to 500-nm-thick enamel hybrid layer (between open arrows) that comprised intact apatite crystallites.

TEM of the resin-enamel interface in Prompt L-Pop (Fig. 3A) revealed two distinct modes of nanoleakage (Tay *et al.*, 2002b) that appeared as isolated silver grains and silver-impregnated water channels (water trees). These pathways for water movement within the adhesive were also seen in the less aggressive adhesive iBond (Fig. 3B), in which the enamel smear layer was retained as part of the hybridized enamel complex (Fig. 3C).

Figs. 4A-4C are clinical photographs documenting the appearance of osmotic blisters after iBond was applied to the labial enamel surface of one co-author. Similar results were also observed with the use of the indirect resin replica technique from impressions taken of another co-author following the application of Xeno III to labial enamel surface (Figs. 4D-4E).

DISCUSSION

Since no water blisters were observed when

specimens were immersed in a concentrated CaCl₂ solution, and pre-existing blisters collapsed after re-immersion in the latter, it appears that the water blisters formed in resin-coated

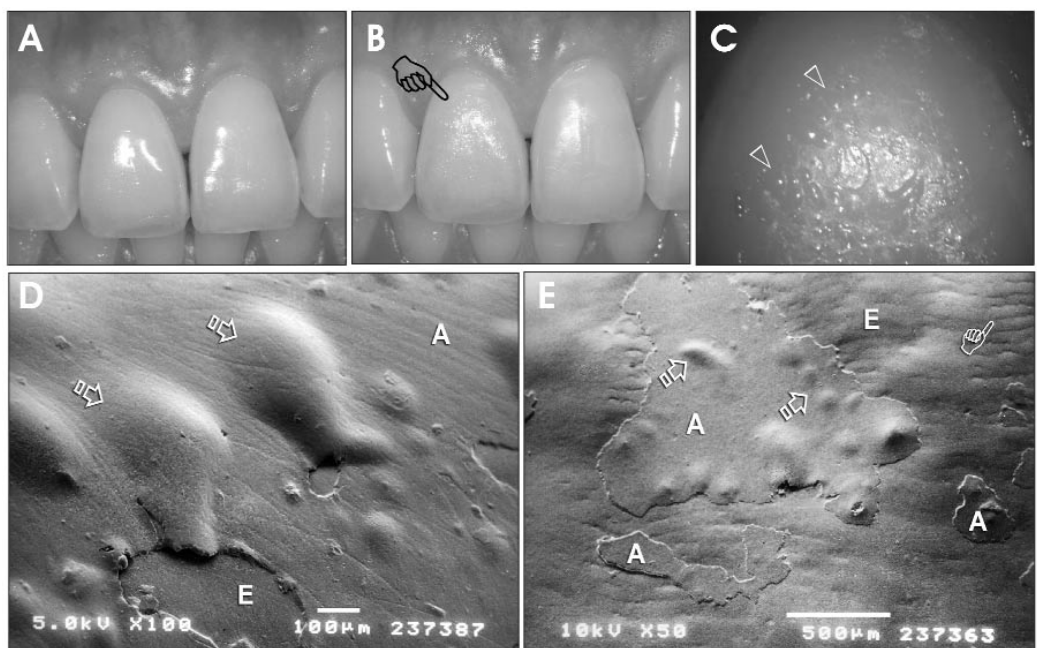


Figure 4. Clinical validation of osmotic blistering in enamel after the application of one-step self-etch adhesives. (A) Photograph of tooth 11 immediately after the application of iBond. (B) The same tooth surface after 1 hr, showing a rough texture (pointer). (C) A high-magnification view of the rough adhesive surface in tooth 11, showing the presence of osmotic blisters (open arrowheads). (D) SEM micrograph of an epoxy resin replica of the enamel surface of tooth 11, reproduced from a polyvinyl siloxane impression that was taken 3 hrs after the application of Xeno III. Osmotic blisters (open arrows) could be observed between the polymerized adhesive (A) and the enamel surface (E). (E) Epoxy resin replica of the same surface 24 hrs after the application of Xeno III. There was almost complete delamination of the adhesive from the enamel surface. Small, undisturbed blisters (open arrows) can still be seen from the fragments of retained adhesive (A). Striae of Retzius (pointer) were evident along the exposed enamel surface (E).

enamel after water immersion were caused by osmosis (Pommersheim and Nguyen, 1998). Although this phenomenon is novel in dentistry, osmotic blistering is the major cause of adhesion loss when a resin-coated substrate (*e.g.*, painted walls) is exposed to high relative humidities (Schwenk, 1981), and such blisters are the initiation sites that precipitate cathodic corrosion of resin-coated metal surfaces (Nguyen *et al.*, 1996b).

The clinical data complemented our *in vitro* observation of osmotic blistering in enamel. Although one-step self-etch adhesives are normally used for coupling with resin composites or luting cements, they may be present as enamel coatings either intentionally or inadvertently. A clinically relevant question is whether non-rinsing self-etch adhesives may be used in lieu of composite surface sealants for refurbishing cavosurface margins in direct and indirect restorations. The results of this study suggest that one-step self-etch adhesives, because of their high water permeability, should not be used for such purposes. Incompletely removed unbound water may exist as water trees (Fig. 1E), providing channels for rapid water movement within the polymerized adhesive (Tay *et al.*, 2002b). Bound water may also exist in the form of primary or secondary hydration shells, due to hydrogen bonding between water molecules and hydrophilic/ionic monomers (Zaikov *et al.*, 1988). These sites were represented by the isolated silver grains (Fig. 1D) and allow for water sorption *via* diffusion into the polymerized adhesive.

In this study, we did not attempt to quantify the number and size of the blisters in different adhesives, since a statistical analysis that involves the comparison of only the physical appearance of these water blisters will not truly reflect the total volume of water that was trapped between the adhesive and enamel (Davies *et al.*, 1983). Quantification of such water movement should be contemplated in future studies, with Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy (Nguyen *et al.*, 1996a), or capacitance measurements of electrical impedance (Wittman and Taylor, 1995), that were used in other branches of science for assessing the water content at the organic coating/substrate interface.

It is remarkable that water blisters can emerge within resin-bonded enamel, despite the relatively strong bonds and enamel hybridization reported when these adhesives were applied to enamel (Pashley and Tay, 2001; Hannig *et al.*, 2002; Ibarra *et al.*, 2002). In this study, we immediately immersed the cured adhesives into different fluid media after light-curing to approximate what could have occurred in the oral cavity after rubber dam removal. FTIR-MIR examination revealed that the degrees of conversion of some of these adhesives were low immediately upon polymerization and that a longer period was required for bond maturation to occur (Mr. Byoung Suh, personal communication). This probably permitted the adhesive to have a relatively high permeability to water. Presumably, during self-etching, the acidic monomers form calcium salts that create a hypertonic environment at the resin-substrate interface. This caused osmosis of water into the hypertonic region. The increased pressure at the interface apparently induced delamination and creep of the resin, resulting in blister formation. Since water could drain away from resin-dentin interfaces through the dentinal tubules, no blister formation occurred, whereas water that accumulated within the relatively impermeable enamel allowed blisters to form with the continuous build-up of osmotic pressure. Nguyen *et al.* (1996a)

further demonstrated that increasing the film thickness of a resin coating only prolonged the time required for water from the outside to reach the resin-substrate interface, but did not completely arrest the process of osmotic blistering. Conversely, the use of multiple coating may help reduce the propensity of osmotic blistering due to the variation in the courses of conductive channels within the different resin layers.

We had initially anticipated the expression of water droplets from bonded dentin (Tay *et al.*, 2002a) following immersion of the specimens in CaCl₂ solution, since water could have been withdrawn from the dentinal tubules through the permeable adhesive layer. However, no water droplets could be seen from bonded dentin. This was probably due to the rapid evaporation of these minute water droplets once the specimens were retrieved from the CaCl₂ solution to be examined by FE-ESEM. Dentin fluid droplets were seen when impressions of both vital and non-vital dentin bonded *in vivo* with one-step self-etch adhesives were examined by a resin replica technique (Chersoni *et al.*, unpublished results). Since no osmotic gradient is generated with the use of a water-insoluble impression material, the driving force for water extrusion from bonded dentin may additionally be caused by the bending moment produced by in-plane compression stresses (*ca.* 5 MPa) created within the film coating after water sorption (Chuang and Nguyen, 1997). It is possible that competition may exist between the osmotic induction of blister growth and the fluid extrusion that is caused by the bending moment created within a swollen adhesive layer, with the former process dominating in enamel and the latter in dentin. While these complex issues should be further clarified in future studies, their manifestations are indirect verification of the permeability that is associated with the use of contemporary one-step self-etch dentin adhesives.

ACKNOWLEDGMENTS

We thank Dr. Doris Au and Michael Chiang, City University of Hong Kong, for the use of the environmental scanning electron microscope and technical assistance. This study was supported by grant 20003755/90800/08004/400/01, Faculty of Dentistry, the University of Hong Kong, and by grant DE 014911 and grant DE 015306 from the NIDCR, USA. The authors are grateful to Zinnia Pang, Kelli Agee, and Shirley Johnson for secretarial support.

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