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Effect of oxygen inhibition in two-step self-etch systems on surface free energy and dentin bond strength with a chemically cured resin composite

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Abstract: We compared the surface free energies and dentin bond strengths of two-step self-etch systems with and without an oxygen-inhibited layer. The adhesives were applied to self-etching primer-treated dentin surfaces of bovine incisors, after which the teeth were light-irradiated and the oxygen-inhibited layer was left intact or removed with ethanol. We determined surface free energies (γ_s) and their components by measuring the contact angles of three test liquids placed on the cured adhesives. We also measured the dentin bond strengths of chemically cured resin composite to the adhesives, with and without the oxygen-inhibited layer. For all surfaces, the estimated surface tension component, γ_s^{LW} , was relatively constant. The Lewis base (γ_s^-) component decreased significantly when the oxygen-inhibited layer was removed, whereas the Lewis acid (γ_s^+) component slightly increased. The dentin bond strengths of the two-step self-etch systems did not significantly differ in relation to the presence of the oxygen-inhibited layer. Although the surface free energy of the adhesive was affected by the presence of the oxygen-inhibited layer, no changes in dentin bond strength were detected. (J Oral Sci 56, 201-207, 2014)

Keywords: two-step self-etch system; oxygen-inhibited layer; dentin bond strength; surface free energy; composites.

Introduction

Because bonding procedures require multistep clinical approaches, the longevity of restorations using adhesive systems may depend on technique-sensitive factors. One- and two-step self-etch application processes have been developed to reduce technique-sensitive factors and achieve optimal bond strength to both enamel and dentin (1). Two-step self-etch systems comprise a self-etching primer and a bonding agent and combine the tooth surface etching and priming steps to treat enamel and dentin simultaneously. Self-etching primer—an aqueous mixture of acidic functional monomers and other constituents—dissolves the smear layer and demineralizes dentin (2).

Light-cured resin composites have superseded chemically cured resin composites in clinical applications because of their ease of use and superior mechanical properties (3). However, chemically cured resin composites are widely used in clinical applications such as core buildups, adhesive luting, and restorations located in areas with poor light penetration (4). Chemically cured resin composites can be used in bulk or as a basal layer to relieve stress resulting from a longer pre-gel phase (5). In addition, use of chemically cured resin composites may facilitate complete polymerization of restorations. These composites have a short working time, but show less

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Table 1 Materials tested

Code	Adhesive (Manufacturer)	Self-etching primer (Lot no.) Main components	Bonding agent (Lot no.) Main components
MB	Clearfil Mega Bond (Kuraray Noritake Dental Inc.)	Primer (250019) MDP, HEMA, water, ethanol, PI, accelerators, dyes	Bond (2R0035) MDP, HEMA, bis-GMA, colloidal silica, PI, accelerators
FB	FL-Bond II (Shofu Inc.)	Primer (111246) carboxylic acid monomer, 6-MHPA, ethanol, water, PI	Bond (111267) HEMA, UDMA, TEGDMA, S-PRG filler, PI
UB	UniFil Bond (GC Corp.)	Primer (130641) 4-MET, HEMA, water, ethanol, PI	Bond (130631) HEMA, UDMA, TEGDMA, filler, PI

MDP: 10-methacryloyloxydecyl di-hydrogen phosphate, HEMA: 2-hydroxyethyl methacrylate, bis-GMA: 2,2bis[4-(2-hydrogen-3-methacryloyloxypropoxy)phenyl]propane, 6-MHPA: 6-methacryloyloxyethyl 3-phosphonoacetate, 4-MET: 4-methacryloyloxyethyl trimellitic acid, UDMA: di(methacryloyloxyethyl)trimethylhexamethylene diurethane, TEGDMA: triethylene glycol dimethacrylate, CQ: *dl*-camphorquinone, S-PRG filler: surface reaction-type pre-reacted glass-ionomer filler, PI: photoinitiator

polymerization stress because of their slower hardening time, which can also optimize interfacial adaptation and decrease postoperative sensitivity. The success of posterior restorations has been attributed to these characteristics.

An oxygen-inhibited layer is created when a resin composite or adhesive resin is polymerized via free-radical polymerization in air (6). Oxygen reacts with carbon-based polymerizing free radicals to form peroxy radicals; consequently, the polymerization reaction is retarded because of the reduced reactivity toward double bonds (7). The oxygen-inhibited layer is composed of unreacted monomers and oligomers and possesses a sticky superficial layer. This layer readily adopts overlying resin composites to increase their contact area and allows materials on both sides to blend, producing a strong chemical bond. Some previous studies (8,9) found that the presence of the oxygen-inhibited layer is required for bonding with resin composites, whereas others reported no significant differences (10,11) or even an inverse correlation (12). Other studies (13,14) reported that the presence of the oxygen-inhibited layer did not affect bonding to newly added resin composite.

Our previous study (15) on one-step self-etch adhesives indicated that the presence of an oxygen-inhibited layer increases dentin bond strength when used with photoinitiators. The relatively thin oxygen-inhibited layer may allow diffusion of overlying light-cured resin composites, resulting in higher bond strengths. Conversely, oxygen inhibition of acidic self-etch adhesives can adversely affect bond strength when combined with chemically cured resin composites (16). Acidic resin monomers in self-etch adhesives may impair polymer-

ization of resin monomers initiated via conventional peroxide-amine binary redox initiators (17,18). The role of the oxygen-inhibited layer on two-step self-etch systems is controversial, and a new modality is necessary in order to determine the effect of this layer on bonding characteristics.

We examined the effect of the oxygen-inhibited layer on surface free energies and dentin bond strengths of two-step self-etch systems when used with a chemically cured resin composite. The null hypothesis was that the presence of the oxygen-inhibited layer has no effect on surface free energies and dentin bond strengths of two-step self-etch systems.

Materials and Methods

Materials tested

The two-step self-etch systems used were Clearfil Mega Bond (Kuraray Noritake Dental Inc., Tokyo, Japan), FL-Bond II (Shofu Inc., Kyoto, Japan), and UniFil Bond (GC Corp., Tokyo, Japan), as listed in Table 1. A chemically cured resin composite, Clearfil FII (Kuraray Noritake Dental Inc.), was used as a restorative.

An Optilux 501 Halogen Curing Light Unit (Kerr Corporation, Orange, CA, USA) was used, and the light intensity (800 mW/cm²) of the curing unit was checked with a dental radiometer (Model 100; Kerr Corporation) before producing the specimens.

Surface free energy

Mandibular incisors from cattle were used as a substitute for human teeth. After removing the roots, the pulp was removed, and the teeth were mounted in self-curing acrylic resin (Tray Resin II; Shofu Inc.) to expose the

Table 2 Surface free energies and parameters of test liquids

Liquid (Lot no.)	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
1-bromonaphthalene* (ALH4513)	43.5	43.5	0.0	0.0	0.0
Ethylene glycol* (KWF0703)	47.9	29.0	18.9	1.9	47.0
Water	72.8	21.8	51.0	25.5	25.5

*: Wako Pure Chemical Industries, Ltd.

Units: $\text{mJ}\cdot\text{m}^{-2}$; subscript L indicates liquid.

γ_L , surface free energy; γ_L^{LW} , Lifshitz-Van der Waals force; γ_L^{AB} , Lewis acid-base interaction; γ_L^+ , Lewis acid; γ_L^- , Lewis base.

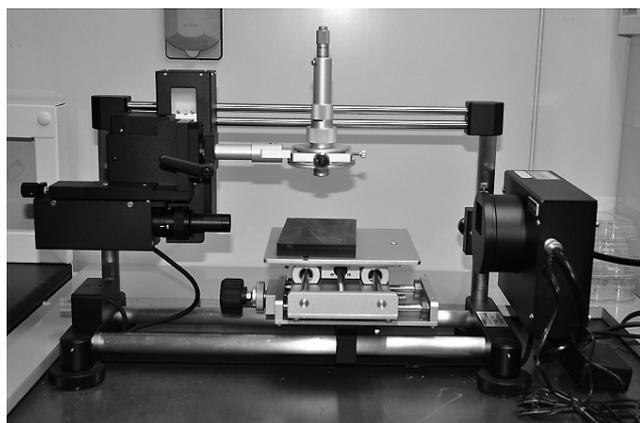


Fig. 1 The Drop Master DM500 was fitted with a charge-coupled device camera. The equilibrium contact angle (θ) of the test liquid was measured using the sessile-drop method.

labial surface of the dentin. The final finish was achieved by grinding the surface with wet 600-grit SiC abrasive paper, followed by washing and drying with oil-free compressed air.

Self-etching primer was applied to the dentin surface for the time periods recommended by the manufacturers. Each treated dentin surface was dried with oil-free compressed air, followed by application of the bonding agent and light irradiation for 10 s. Specimens were used for contact angle measurements with or without the oxygen-inhibited layer. The top surface of the adhesive was removed with an ethanol-impregnated cotton pad to produce specimens without an oxygen-inhibited layer.

Surface free energy was determined by measuring the surface contact angle for three test liquids: distilled water, ethylene glycol, and 1-bromonaphthalene (19). A Drop Master DM500 (Kyowa Interface Science Co., Ltd., Saitama, Japan) fitted with a charge-coupled device camera was used for automatic measurements of contact angles (Fig. 1). The equilibrium contact angle was measured using the sessile-drop method for five specimens of each two-step self-etch system. Parameters of surface free energy were calculated using add-on software (FAMAS; Kyowa Interface Science Co., Ltd.),

based on the fundamental concepts of wetting (20).

Dentin bond strength

A piece of double-sided adhesive tape with a hole (diameter, 4 mm) was attached to the dentin surface. After application of self-etching primer, bonding agent was applied to the dentin surface and light-irradiated for 10 s. The surface of the adhesive was removed with an ethanol-impregnated cotton pad to produce specimens without an oxygen-inhibited layer. A Teflon mold (height, 2 mm; diameter, 4 mm) was used to shape the resin composite and secure it on the dentin surface. The mold was firmly attached to the double-sided adhesive tape, and the mixed resin composite was condensed into the mold. The finished specimens were transferred to distilled water and stored at 37°C for 24 h.

Ten specimens per group were tested using a shear knife-edge testing device (Type 4204; Instron, Norwood, MA, USA) at a crosshead speed of 1 mm/min. Shear bond strength was calculated as peak load at failure divided by the surface area of the specimens. After testing, the specimens were examined to identify the location of the failure. Failure was classified as adhesive failure if it occurred between the dentin and the composite and as cohesive failure if it occurred in the composite or dentin.

Statistical analysis

Data for each group were tested for homogeneity of variance using Bartlett's test. Student's *t* test was used to compare differences according to the presence or absence of the oxygen-inhibited layer at a significance level of $\alpha = 0.05$. One-way analysis of variance followed by Tukey's honestly significant difference test were also used to compare adhesive systems ($\alpha = 0.05$). All statistical analyses were performed using SigmaStat 3.1 (SPSS Inc., Chicago, IL, USA).

Scanning electron microscopy

Bonded specimens in each group were stored in distilled water at 37°C for 24 h and then embedded in self-curing epoxy resin. Embedded specimens were sectioned, and

Table 3 Surface free energies and parameters of cured adhesive surfaces

Adhesive	Oxygen inhibition	γ_s	γ_s^{LW}	γ_s^{AB}	γ_s^+	γ_s^-
Clearfil Mega Bond	Present	41.1 (5.3)	41.1 (1.1)	0.0 (0.0)	0.0 (0.0)	27.4 (3.7)
	Absent	47.8 (2.3)	41.4 (0.8)	6.4 (2.2)	1.1 (0.5)	9.3 (4.7)
FL-Bond II	Present	42.0 (0.6)	42.0 (0.6)	0.0 (0.1)	0.0 (0.0)	44.4 (3.8)
	Absent	47.5 (1.1)	42.9 (0.2)	4.6 (1.2)	0.2 (0.1)	26.2 (1.5)
UniFil Bond	Present	42.6 (0.5)	42.6 (0.5)	0.0 (0.1)	0.0 (0.0)	47.4 (4.3)
	Absent	50.0 (1.1)	43.0 (0.4)	7.0 (1.0)	1.0 (0.2)	12.1 (2.4)

Units: $\text{mJ}\cdot\text{m}^{-2}$; subscript S indicates solid; values in parentheses are standard deviations ($n = 5$).

γ_s , surface free energy; γ_s^{LW} , Lifshitz-Van der Waals force; γ_s^{AB} , Lewis acid-base interaction; γ_s^+ , Lewis acid; γ_s^- , Lewis base.

Values connected by lines do not significantly differ (Student's t test, $P > 0.05$).

Table 4 Effect of the oxygen-inhibited layer on dentin bond strength with chemically cured resin composite

Oxygen inhibition	Clearfil Mega Bond	FL-Bond II	UniFil Bond
Present	9.7 (2.4) ^a	11.8 (3.0) ^a	10.4 (3.2) ^a
[Fracture mode]	[10/0/0]	[10/0/0]	[10/0/0]
Absent	11.5 (3.1) ^a	12.5 (2.8) ^a	11.3 (2.5) ^a
[Fracture mode]	[10/0/0]	[10/0/0]	[10/0/0]

$n = 10$; values in parentheses indicate standard deviations.

Failure mode is shown as [adhesive failure/cohesive failure in resin/cohesive failure in dentin].

Values with the same superscript letters do not significantly differ (Tukey's honestly significant difference test, $P > 0.05$).

the surfaces of the cut halves were polished using SiC abrasive papers with grit sizes of 600, 1,200, and, 4,000, successively (EcoMet 4/AutoMet 2; Buehler Ltd., Lake Bluff, IL, USA). The surface was finally polished on a soft cloth using diamond paste with a grit size of 1 μm . All specimens were dehydrated in ascending concentrations of 2-methyl-2-propanol (50% for 20 min, 75% for 20 min, 95% for 20 min, and 100% for 2 h), then transferred to a critical-point dryer. Their surfaces were subjected to Ar ion beam etching (Type EIS-200ER; Elionix Co., Ltd., Tokyo, Japan), then coated with a thin film of Au in a vacuum evaporator (Quick Coater Type SC-701; Sanyu Denshi Inc., Tokyo, Japan) for observation by scanning electron microscopy (SEM; ERA 8800FE; Elionix Co., Ltd.).

Results

The surface free energies and their components in cured adhesives are shown in Table 3. Total surface free energy (γ_s) values were significantly higher when the oxygen-inhibited layer was removed. For all surfaces, γ_s^{LW} values remained relatively constant, at 41.1-43.0 $\text{mJ}\cdot\text{m}^{-2}$. The γ_s^+ component values increased slightly when the oxygen-inhibited layer was removed, whereas γ_s^- component values decreased significantly. The values of the acid-base interaction (γ_s^{AB}) component increased

from 0 to 4.6-7.0 $\text{mJ}\cdot\text{m}^{-2}$ when the oxygen-inhibited layer was removed.

The shear bond strengths of the light-cured resin and chemically cured resin composites with or without the oxygen-inhibited layer are shown in Table 4. Regarding the bonding of resin composites, there were no significant differences between specimens with and without the oxygen-inhibited layer. Failure type was not associated with bond strength: the predominant failure type was adhesive failure, irrespective of the presence of the oxygen-inhibited layer.

SEM observations of the resin-dentin interface are shown in Fig. 2. Although the thickness of the adhesive resin differed in each group, the resin-dentin interface in all groups showed good adaptation between the adhesive resin and dentin substrate.

Discussion

Two-step self-etch systems were developed to simplify and shorten bonding procedures. Self-etching primers form a continuous layer between the resin composite and tooth substrate, simultaneously demineralizing the dentin with acidic functional monomers and allowing the penetration of adhesive resin into the primed tooth surface (21). The oxygen-inhibited layer is present on the surface of adhesive resins and contains bifunctional monomers

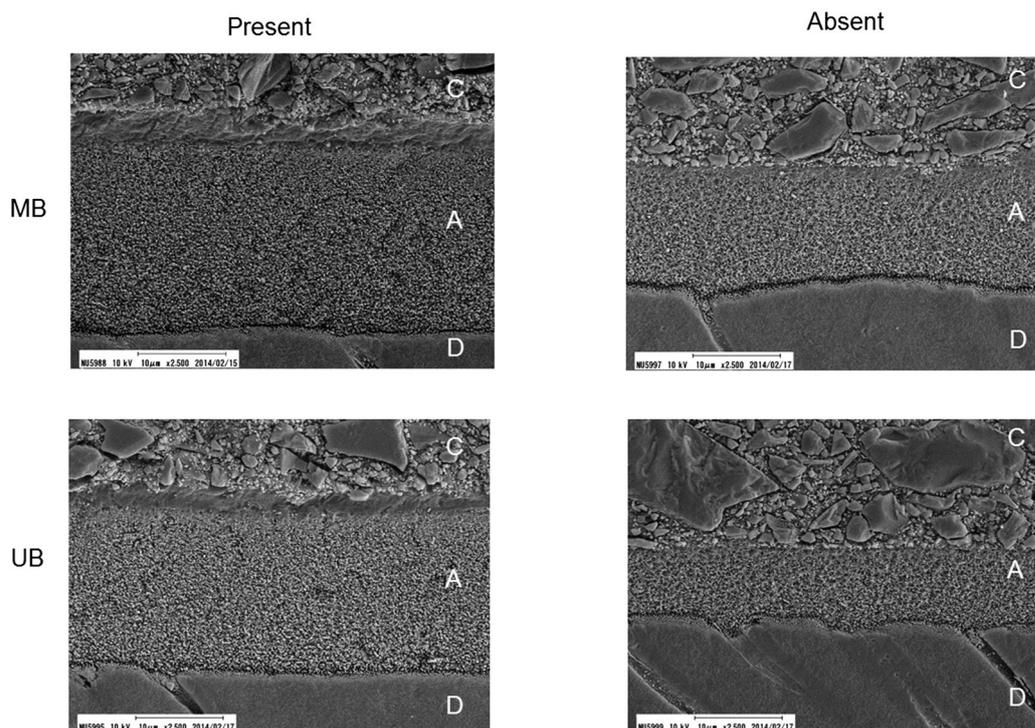


Fig. 2 Representative scanning electron microscopy images of the Clearfil FII-dentin interface (original magnification, $\times 3,000$; C: resin composite; A: adhesive; D: dentin). The resin-dentin interface in each group showed excellent adaptation between the adhesive resin and dentin substrate.

and acidic functional monomers with carboxylic or phosphate ester groups. It is assumed that interaction occurs between residual acidic resin monomers in the oxygen-inhibited layer and binary peroxide-amine catalytic components of chemically cured resin composites.

In the present study, to understand the compatibility between two-step self-etch systems and chemically cured resin composites, we investigated the surface free energies of adhesive resins. The Lewis acid-base properties of resinous materials influence their interfacial interactions with liquids capable of forming hydrogen bonds (22). According to a theory proposed by Fowkes (23), the acid-base properties of solids can be quantitatively characterized using interface chemistry. On the basis of the theory of interfacial interactions, surface energy is assumed to comprise two components: non-polar forces and acid-base interactions (22). Interactions between phases across interfaces and the forces acting between molecules should be considered for optimal bond strength during dentin bonding.

Optimal wettability is also important for enabling adhesive material to spread across the adherent surface and establish bonding (24). Factors that influence the wetting of a solid by a liquid include the surface tension of the liquid and the surface free energy of the solid (γ_s). To achieve optimal wettability, the surface free energy of the

solid must be maximized, and the liquid should exhibit a low angle of contact with the solid (25). Variation in the wettability of different adhesive resins is influenced by Lewis acid-base interactions. The Lewis acid component (γ^+) interacts with the Lewis base component (γ^-), and these interactions determine the wettability of cured adhesive resins. Specimens with an oxygen-inhibited layer have lower γ_s values than do specimens without this layer. In aqueous media, the γ_s^{AB} interfacial terms mainly comprise interactions between hydrogen donors and hydrogen acceptors and between electron acceptors (γ^+) and electron donors (γ^-). Removal of the oxygen-inhibited layer significantly increases γ_s^{AB} , which leads to significantly higher γ_s values. The γ_s^{LW} value was unaffected by the presence of the oxygen-inhibited layer; however, γ_s^- values were higher in specimens with an oxygen-inhibited layer than in those without such a layer. Because of the hydrophilic and hydrophobic properties of functional monomers, the oxygen-inhibited layer may act as a Lewis base.

Our results indicate that the presence of an oxygen-inhibited layer does not significantly affect bond strength between chemically cured resin composites and two-step self-etch adhesive systems. Aromatic sulfinic acid sodium salts are incorporated into adhesives to improve their polymerization in the presence of acidic monomers

(26). Because of the presence of sulfinic acid sodium salts and the reduced concentrations of acidic functional monomers in adhesive resins, adverse interactions are not believed to occur between acidic monomers and the polymerized catalysts of chemically cured resin composites. One polymerization initiator commonly used with chemically cured resin composites is a redox initiator system consisting of benzoyl peroxide (BPO) and nucleophilic tertiary amines. Aromatic tertiary amines (electron acceptors) react with the acidic groups (electron donors) of adhesive monomers, forming charge-transfer complexes that impede free-radical generation, resulting in incomplete polymerization of chemically cured resin composites (27). To overcome this incompatibility, use of BPO-aromatic tertiary amine-*p*-toluenesulfinic acid sodium salts with an acidic phosphate monomer has been proposed (28). Together, they function by replenishing free radicals depleted from the tertiary amines of chemically cured resin composites by reacting with residual acidic monomers in the oxygen-inhibited layer of adhesive resins. If the acidic monomer concentration is increased, uncured acidic monomers may diffuse into the overlying resin composite and react with the aromatic tertiary amine co-initiator (Lewis base) in the composite, preventing its polymerization at the interface (29).

Although bond strength did not significantly differ between specimens with and without an oxygen-inhibited layer, changes in surface free energy were evident. Even after removal of the oxygen-inhibited layer, a low-polymerization layer remained on the surface of the cured adhesive resin, containing uncured C=C double bonds ready to react with newly added resin composite. Reportedly (30), there is no correlation between bond strength and the calculated work of adhesion (W_A) because W_A is a measure of energy, whereas bond strength is a measure of stress. However, there are other possible explanations of the relationship between surface free energy and bond strength.

In conclusion, we showed that the presence of the oxygen-inhibited layer in two-step self-etch systems had an effect on surface energy but not on dentin bond strength with a chemically cured resin composite. Future research should examine the effects of functional monomers and confirm that the present findings are consistent with clinical performance.

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Conflict of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

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