Masters of Esthetic Dentistry

OXYGEN-INHIBITED LAYER IN ADHESION DENTISTRY

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PROFILE

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SungKyun Kwan University, Seoul, South Korea, 1960, BS Chemistry
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Honor/Award
American Academy of Cosmetic Dentistry (AACD) 2003 Presidential Award for Outstanding Contribution to the Art and Science of Cosmetic Dentistry

Publications
19 articles, most notably articles published in *Journal of Esthetic Dentistry, Compendium, American Journal of Dentistry,* and *Journal of Adhesive Dentistry*

Contributions to Dentistry
22 patents, including 1991 fluoride release agent copolymer prepared using morpholinoethyl methacrylate hydrofluoride comonomer, 1994 dentin bonding system, 1995 antimicrobial etchants, 1997 one-component primer/bonding-resin systems, 1999 flexible dental composite compositions and restorative methods using flexible dental compositions
22 patents pending, including BisCover—the newest innovation in dentistry

Personal Interests
Golf, tennis

ABSTRACT

Purpose: Characteristics of the oxygen-inhibited layer, including bond strength, photoinitiator decomposition, and post-curing degree of conversion, were investigated.

Materials and Methods: To investigate shear bond strength, BisCover (Bisco, Inc., Schaumburg, IL, USA) and D/E Resin (Bisco, Inc.) were placed on disks of Renew composite (Bisco, Inc.) and cured both with and without an oxygen-inhibited layer. Light-Bond composite (Reliance Orthodontic, Itasca, IL, USA) was placed in a gelatin capsule and light cured over the cured resin. After soaking in water for 2 hours at 37°C, specimens were sheared to failure using a universal testing machine (Model 4466, Instron Inc., Canton, MA, USA).

To investigate microtensile bond strength, composite substrates prepared using Renew A2 composite were light cured either in air or under nitrogen. Light-Core (Bisco, Inc.) was placed on each substrate and light cured. The resulting specimens were sectioned into composite beams and stressed to failure using a microtensile tester (built by Bisco, Inc.).

To determine camphorquinone (CQ) decomposition, an experimental CQ resin was placed between two glass plates and irradiated for different time intervals. The absorption spectrum was obtained using a Cary 50 Bio UV-Visible Spectrometer (Varian, Mulgrave, Australia).

To explore the degree of conversion, polyester film strips (Mylar, DuPont, Wilmington, DE, USA) coated with the CQ resin were pre-cured in air for different time periods, and then post-cured at low intensity for 5 minutes under nitrogen. A Spectrum 1000FTIR Spectrometer (Perkin Elmer, Norwalk, CT, USA) was used to measure the degree of conversion.

Results: Bond strength tests resulted in no significant difference between samples with or without an oxygen-inhibited layer. The oxygen-inhibited layer contained reduced amounts of photoinitiator. The degree of conversion of post-cured oxygen-inhibited layers was lower than that for the control.

Conclusion: An oxygen-inhibited layer is not necessary for bonding with composite resin.

CLINICAL SIGNIFICANCE

It was believed that an oxygen-inhibited layer was required for bonding of composite resin. Studies show that composites bond even in the absence of an oxygen-inhibited layer, including recent products that cure without an oxygen-inhibited layer. With many simplified adhesives, especially self-etching, all-in-one adhesives, the oxygen-inhibited layer is acidic. This acidity interferes with self-curing reactions, making these adhesives incompatible with self-cured composites.

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Light- or chemically cured dental composite resins leave a soft, sticky superficial layer upon polymerization. This layer is commonly referred to as an oxygen-inhibited layer because of its origin, and it is always present when a composite or bonding resin is polymerized in air. For years the dental community has held a common perception that an oxygen-inhibited layer is required before adding more layers of bonded composite. Based on the principle of molecular interaction, one might easily reason that an oxygen-inhibited layer should improve the interfacial bonding between two contacting polymers.[1] The oxygen-inhibited layer is primarily composed of unreacted monomers and oligomers,[2] and it possesses a liquid-like consistency. This layer not only readily adopts the overlying material to increase the contacting area, it also allows the materials on both sides to cross the interface and blend together to form an interdiffused zone, where copolymerization can take place to produce a chemical bond. All of these actions would tend to strengthen the layer-layer interaction.

I reviewed the scientific literature and found nine research papers addressing the subject of the oxygen-inhibited layer and bonding.[3–11] Reports on how the oxygen-inhibited layer affects bond strength have been inconsistent, despite many efforts dedicated to the subject. Three articles described a positive correlation, indicating that the oxygen-inhibited layer increased bond strength.[3–5] Two articles reported that the presence of an oxygen-inhibited layer made no significant differences in bond strength.[6,7] Four articles, however, concluded that the presence of an oxygen-inhibited layer was, in fact, detrimental to bonding additional layers of composite.[8–11]

Articles by Rueggeberg and Margeson and by Eliades and Caputo both presented convincing data along with supporting experiments against the common perception relating to the oxygen-inhibited layer.[8,10] In general, they found higher bond strengths when bonding to a surface that was cured in an inert atmosphere (argon) or to a surface that was cured after removing the oxygen-inhibited layer from the composite with acetone.[10] Eliades and Caputo explained their results by observing that the resin in the oxygen-inhibited layer has the same composition as the uncured resin, except that the photoinitiator system, commonly camphorquinone (CQ) and amine, has been consumed or decomposed.[10] The photoinitiator-deprived, oxygen-inhibited layer therefore interferes with the formation of a perfect bond (polymerization) with the overlying resin composite.

Rueggeberg and Margeson reported the following: (1) the thickness of the oxygen-inhibited layer of a resin (Command, Kerr Corporation, Orange, CA, USA) was 37 ± 16 μm; (2) the degree of conversion was the highest when the resin was cured in an argon atmosphere; (3) the degree of conversion of an oxygen-inhibited layer was not improved by an additional 40 seconds of light-curing time through a 1.5 mm thick composite disk (Herculite XR, Kerr Corporation); and (4) the degree of conversion improved when cured with a layer of fresh composite, but not to the level achieved in an argon atmosphere.[8]

The common perception that an oxygen-inhibited layer is needed for bonding now appears to be wrong. During the development of BisCover (Bisco, Inc., Schaumburg, IL, USA), a resin that cures without an oxygen-inhibited layer, Suh and colleagues investigated the possibility of bonding orthodontic brackets to BisCover cured on enamel, where it was used to protect the enamel from decalcification.[12] The results of this investigation showed that one actually can add additional layers of bonded composite to a surface that does not exhibit an oxygen-inhibited layer. This article presents the result of this study in greater detail.

Rueggeberg and Margeson found that monomer conversion values after an initial light cure did not increase with an additional light activation through a wafer of cured composite, indicating that additional light curing of already cured, unfilled resin does not cause additional polymerization.[8] This result can be attributed to the fact that the photoinitiator (CQ-amine) has been consumed or decomposed significantly during the initial phase of light activation, as described by Eliades and Caputo.[10] The current article also addresses the levels of photodecomposition and degree of conversion of the oxygen-inhibited layer.

The following interrelated hypotheses were considered:

1. The oxygen-inhibited layer is not necessary for the bonding of composite resins.
2. The oxygen-inhibited layer contains a reduced amount of photoinitiator.
3. The degree of conversion of the oxygen-inhibited layer is adversely affected by this reduced amount of photoinitiator.

MATERIALS AND METHODS

A VIP halogen curing light (Bisco, Inc.) at 500 mW/cm^2 was used throughout the testing methods described in this section, unless otherwise specified.

Shear Bond Strength Test

A disk (1 cm diameter) of Renew hybrid composite (Bisco, Inc.) embedded in acrylic was used as a bonding substrate; the surface was sandblasted, rinsed, and dried. BisCover and D/E Resin of All-Bond 2 (both from Bisco, Inc.) were used as the bonding resins, prepared with and without an oxygen-inhibited layer. To prepare the BisCover specimen with an oxygen-inhibited layer, the BisCover was cured for only 5 seconds. For the D/E Resin specimen without an oxygen-inhibited layer, the D/E Resin was cured under a nitrogen atmosphere for 20 seconds. A light-cured composite material (Light-Bond, Reliance Orthodontic, Itasca, IL, USA) was placed in a no. 5 gelatin capsule and immediately placed over the cured resin for each specimen; it was then light cured after excess material was removed. After being stored for 2 hours in deionized water at 37°C, specimens were sheared to failure using an universal testing machine (Model 4466, Instron Inc., Canton, MA, USA) at a crosshead speed of 5 mm/min. The bond strength was calculated from the maximum force recorded.

Microtensile Bond Strength Test

A composite substrate (10 mm diameter, 5–6 mm thick) was prepared in three increments using Renew A2 translucent light-cured composite in air for testing with the oxygen-inhibited layer. Each layer (1.5–2 mm) was light cured for 40 seconds. Light-Core (Bisco, Inc.), tinted blue for test purposes, was placed on the Renew substrate in three increments, with each increment light cured for 40 seconds. The result was a composite-composite specimen (10–12 mm thick) with an oxygen-inhibited layer interface. A second specimen was prepared in much the same way as the first, except that the final increment of Renew was cured under a dry nitrogen atmosphere so that there was no visible oxygen-inhibited layer at the composite interface.

Each composite-composite specimen was sectioned into 0.9 mm wide serial slabs using an Isomet saw (Buehler Ltd., Lake Bluff, IL, USA) under water cooling. The slabs were further sectioned into 0.9 × 0.9 beams using the "nontrimming" version technique of the microtensile bond test.[13] The resulting composite beams (0.9 × 0.9 × 10 mm) were fixed on a microtensile tester (built by Bisco) and stressed to failure in tension mode. The bond strength was calculated from the maximum force recorded.

TABLE 1. SHEAR BOND STRENGTHS OF COMPOSITE TO RESIN-COATED COMPOSITE.

Coated Resin	With O_2 Layer (MPa)	Without O_2 Layer (MPa)	No. of Specimens
BisCover	19.9 (2.9)*	20.8 (3.3)	10
D/E Resin	18.6 (3.5)	22.8 (4.8)†	10

*Undercured intentionally.
†Cured under nitrogen.

CQ Decomposition

An experimental resin was prepared by dissolving CQ (0.3%) and ethyl 4-dimethylaminobenzoate (EDMAB) (0.3%) in a blend of 62:38 dimethacrylate–triethylene glycol dimethacrylate (TEGMA). (Hereafter, this is referred to as the CQ resin.) The CQ resin was placed between two glass plates and irradiated at 500 mW/cm^2 for different time intervals ranging from 0 to 100 seconds. The absorption spectrum for each sample was obtained using a Cary 50 Bio UV-Visible Spectrometer (Varian, Mulgrave, Australia).

Degree of Conversion

The CQ resin was coated on a polyester film strip (Mylar, DuPont, Wilmington, DE, USA) placed on a cured composite disk of A2 shade as a background. The film was precured in air with a halogen lamp at 600 mW/cm^2 for 0 (control), 10, 20, and 40 seconds. The oxygen-inhibited layer of each pre-cured specimen was then irradiated (post-cured) at a low intensity (20–30 mW/cm^2) for 5 minutes under an N_2 atmosphere. The low intensity of light was used to simulate a clinical situation of a buildup of layers of composite, that is, when the first cured layer is covered with a second layer of 1.5 to 2.0 mm of composite. A Spectrum 1000FTIR Spectrometer (Perkin Elmer, Norwalk, CT, USA) with a Golden Gate single-reflection diamond ATR (P/N 10500 series, Graseby Specac, Smyrna, GA, USA) was used to measure the degree of conversion. The spectrum was taken, and the extent of double bond conversion was calculated using the ratio of aliphatic peak heights before and after the irradiation.

RESULTS AND DISCUSSION

Bond Strength

The shear bond strength values of composite bonded to BisCover and D/E Resin, both with and without an oxygen-inhibited layer, were measured (Table 1). In all cases, the fracture mode of the fractured surfaces revealed substrate composite fractures, indicating that the bonds to both the BisCover and D/E Resin were stronger than the substrate itself.

Microtensile bond strengths of composite bonded to composite (Renew) were also measured for samples with and without an oxygen-inhibited layer and exhibited no significant difference (Table 2). An examination of the fractured surfaces by scanning electron microscope also showed no difference between the tested samples. The sample cured under nitrogen showed a cohesive fracture mode between the substrate and layered (overlaid) composite, indicating that a strong bond was formed, even without an oxygen-inhibited layer at the interface (Figures 1 and 2).

There appears to be a discrepancy between the previous findings from the literature (that bond strengths were lower with oxygen-inhibited layer) and the results reported above (that there is no difference with or without an oxygen-inhibited

TABLE 2. MICROTENSILE BOND STRENGTHS COMPOSITE TO COMPOSITE.

Curing Conditions	Bond Strength (MPa)	No. of Specimens
O_2 (with O_2 layer)	70.2 (16.7)	55
N_2 (without O_2 layer)	69.2 (13.9)	46

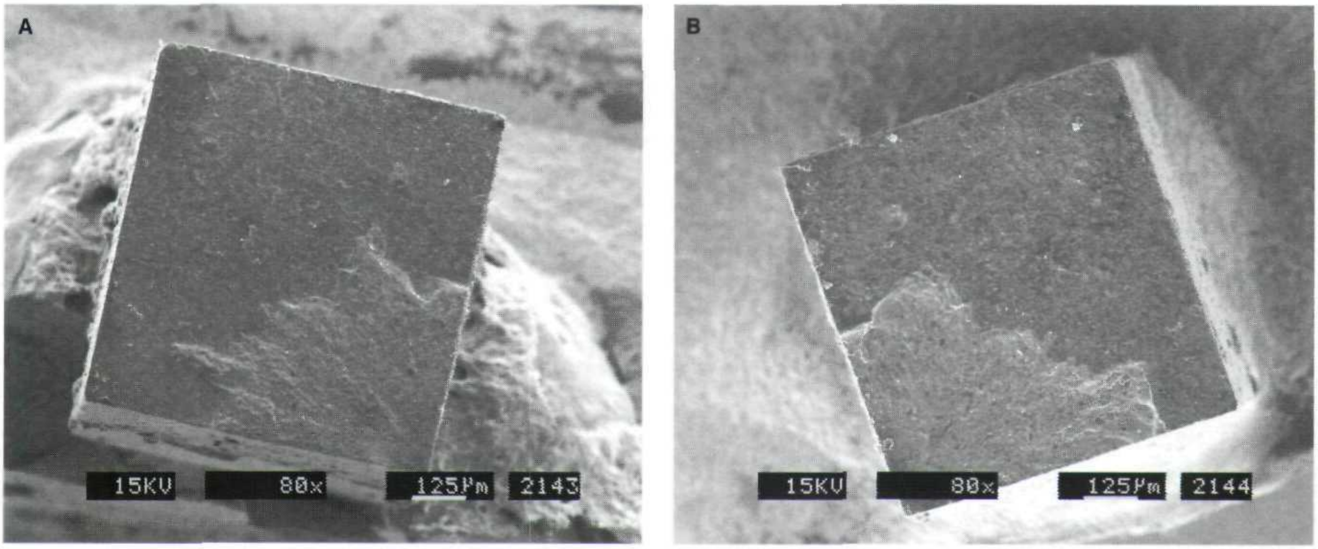

Figure 1. Low-magnification scanning electron micrographs of fractured surfaces after microtensile bond test for sample cured under nitrogen (fracture occurred at 86.8 MPa). Note the broken interfaces from the left (A) and right (B) halves of the substrate specimen (×80 original magnification).

layer). The extremely high thickness of the oxygen-inhibited layer (37 ± 16 μm) reported by Rueggeberg and Margeson may have prevented effective interdiffusion of fresh composite (photoinitiator) into the inhibited layer, resulting in underpolymerization and lower bond strength.[8] However, with the advancements in photoinitiators used in the latest resin formulations, the thickness of the oxygen-inhibited layer was recently measured to be much less than 6 μm (Bisco data on file). With a lower thickness of oxygen-inhibited layer, it is possible to completely interdiffuse the oxygen-inhibited layer with fresh composite overlay, resulting in a normal bond strength.

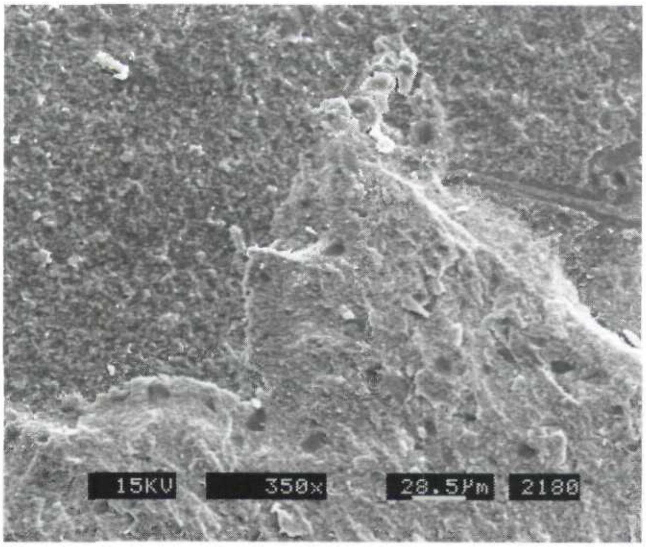

Figure 2. High-magnification view of the image in Figure 1A shows a cohesive fracture mode between the substrate and layered (overlaid) composite (×350 original magnification).

CQ Decomposition

The level of CQ remaining in the CQ resin after curing was measured by its relative absorbance in the ultraviolet-visible spectrum (Figure 3). The height of CQ absorption band (at 468 nm) of the CQ resin decreased as curing time increased. After 100 seconds of irradiation at 500 mW/cm^2, the CQ band absorbance was almost nonexistent.

The relative rate of CQ decomposition can be shown by plotting the

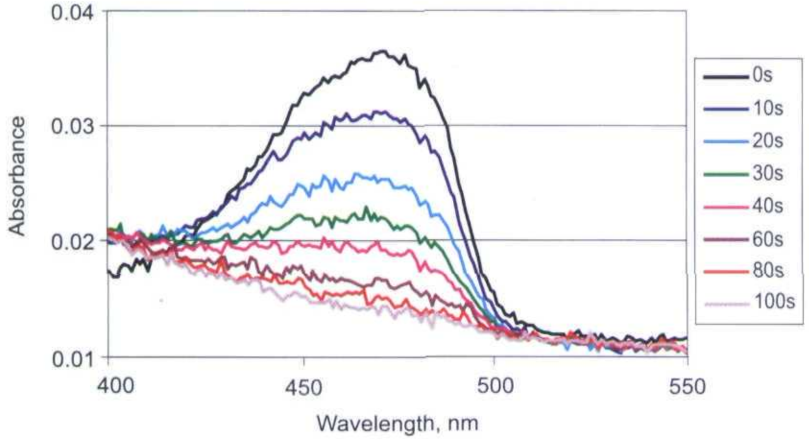

Figure 3. Photodecomposition of camphorquinone (CQ) (0.3%) in the presence of an amine as co-catalyst in an unfilled resin (dimethacrylate [62%] + triethylene glycol dimethacrylate (TEGMA) [38%]) as a function of irradiation time with a halogen lamp at 500 mW/cm². The absorbance of CQ decreases as the curing time increases.

relative peak height at 468 nm against the irradiation time (Figure 4). From the results, it can be approximated that 50% of the CQ is decomposed after 23 seconds of irradiation at 500 mW/cm².

The same experiment was repeated for various light intensities (100–600 mW/cm²) used to cure the CQ resin. The rate of CQ decomposition was found to be irradiation energy dependant. A comparison of results showed that the CQ half-life decreases with higher-intensity irradiation (Figure 5).

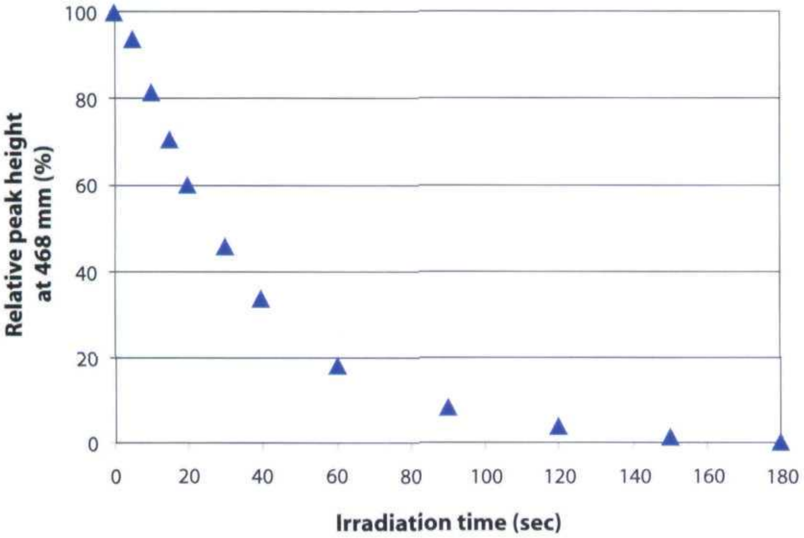

Figure 4. Rate of camphorquinone (CQ) decomposition, based on the relative absorbance peak height of CQ at 468 nm versus irradiation time at 500 mW/cm². The CQ half-life can be interpolated from the results.

Degree of Conversion

If a reduced amount of photoinitiator is present, the resin in an oxygen-inhibited layer may not be cured well upon subsequent irradiation without the diffusion of fresh CQ from overlying composite layers. Results showed that the degree of conversion of the oxygen-inhibited layer decreased with an increased pre-curing time (Table 3). These results further indicate that the oxygen-inhibited layer contains significantly reduced levels of CQ photoinitiator. They also imply that a long curing time may negatively impact the ability of the oxygen-inhibited layer to be post-cured.

Detrimental Oxygen-Inhibited Layer of Acidic Adhesives

With the development of many simplified two-step and single-step adhesives, an acidic oxygen-inhibited layer is inevitable owing to their inherent acidity, especially with self-etching, all-in-one adhesives. However, an acidic oxygen-inhibited layer may considerably reduce bond strength in particular instances.

Many studies have shown an incompatibility (lower bond strength) between acidic adhesives and self-cured composites such as core buildup materials and luting composites.[14–16] A simple explanation for the lower bond strengths with

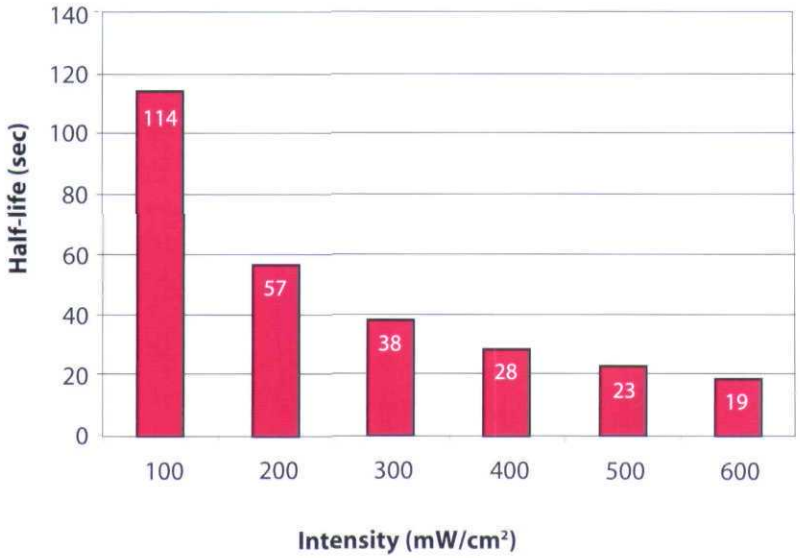

Figure 5. The half-life in seconds of camphorquinone (CQ) for various irradiation intensities. CQ has a shorter half-life at higher curing intensities.

self-cured composites is that the acid present in the oxygen-inhibited layer of the single-step adhesives comes into contact with the self-cured composite in the intermixed zone. There, the uncured acid reacts with the aromatic tertiary amine co-initiator (Lewis base) of the self-cured composite and deactivates it via an acid-base reaction, preventing the adequate polymerization of the self-cured composite at the interface and resulting in poor or no bond strength.[17] This phenomenon is commonly referred to as adhesion incompatibility.

TABLE 3. POST-CURE DEGREE OF CONVERSION AS A FUNCTION OF PRECURE TIME.

	Precure Time (s)			
	0	10	20	40
DC (%)	48.3	43.1	36.3	32.3
% reduction in DC	0	10.8	25.1	33.1

DC = degree of conversion.

TABLE 4. BOND STRENGTH OF XENO III* IN DIFFERENT SUBSTRATES AND CONDITIONS.

Substrate	Curing Condition of Adhesive	Composite Type	Microtensile Bond Strength (mTBS) (MPa)
Dentin	Air (oxygen)	Light cured	52.1 ± 10.3
Dentin	Air (oxygen)	Self-cured	11.9 ± 4.8
Composite	Air (oxygen)	Self-cured	52.8 ± 9.8
Composite	Nitrogen (no oxygen)	Self-cured	57.6 ± 8.0

Adapted from King N et al,[18] and Suh BI et al.[19]
*Self-etching (acidic), single-step adhesive.

Two International Association of Dental Research abstracts on adhesion incompatibility profiles also support the fact that an oxygen-inhibited layer is not necessary for good bonding of a composite.[18,19] When a self-etching (acidic), single-step adhesive such as Xeno III (Dentsply/Caulk, Milford, DE, USA) was cured on a composite substrate in air (oxygen-inhibited layer present) or in nitrogen (no oxygen-inhibited layer present) and bonded with a self-cured composite, there was no difference in bond strengths (Table 4). This demonstrates the fact that a good composite bonding can be achieved without an oxygen-inhibited layer. The low bond strength to dentin with a self-cured composite also demonstrates the adverse effect of an acidic oxygen-inhibited layer to a self-cured composite, although it is also affected by the permeability of self-etching adhesives.[16]

CONCLUSIONS

Based on a review of the literature and current research, it can be concluded that an oxygen-inhibited layer is not necessary for bonding with composite resin, dispelling common perceptions to the contrary. In fact, the presence of an oxygen-inhibited layer in acidic, self-etching adhesives results in their incompatibility with self-cured composites.

A substantial amount of photoinitiator (CQ) can be photodecomposed in the oxygen-inhibited layer of a resin composite or an unfilled resin after light cure. Such a depletion is likely to result in a lower degree of conversion for this layer. Therefore, care should be taken not to overcure the sublayers of a composite or bonding agent. Doing so will conserve the initiator in the oxygen-inhibited layer, thus providing sufficient initiation to well cure the interfaces between layers.

DISCLOSURE

The author is president and owner of Bisco, Inc.

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