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실란이 포함된 접착제와 실란을 별도로 사용한 접착제의 실리카 기반 세라믹 접착 효과

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Effect of silane incorporated adhesive or adhesive using separate silane on bonding of silica-based ceramics

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본 연구의 목적은 실란(silane)이 포함된 유니버설 접착제(universal adhesive)와 실란을 별도로 사용하는 접착제의 실리카 기반 세라믹의 접착력 차이를 평가하는 데에 있다. 리튬 다이실리케이크 기반에 세라믹 재료인 IPS e-max에 대한 표면처리제로서의 각각의 효과를 평가하기 위해 1) All-Bond Universal (ABU), 2) 실란을 실험목적으로 ABU와 섞은 물질, 3) 포세린 프라이머, 4) 실란을 성분으로 함유하고 있는 Scotch Bond Universal을 고려하였다. 접촉각 시험과 전단 결합 강도 실험을 진행하였으며, 이 때 전단 결합 강도에서는 시편을 연마한 상태로 사용함으로써 기계적인 결합력을 배제하였다. 실험 결과 실란을 따로 사용한 시편에서 높은 접촉각과 전단 결합 강도가 측정되었고, 실란은 소수성의 레진과 분리되어 사용되는 것이 표면처리제로서의 기능이 더 효과적인 것으로 나타났다. 결론적으로 실란은 소수성의 레진과 섞어서 사용 된다면 순수한 실란 만큼의 표면처리 효과를 기대하기 어려우며 실란의 임상적 사용에 있어서 순수 실란의 사용이 효과적인 표면 처리제로서의 작용을 하므로 접착제와 분리된 제품을 사용하는 것이 유리함을 확인하였다.

색인단어 : 실란, 유니버설 접착제, 표면 처리, 실리카 기반 세라믹, 리튬 다이실리케이트

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Introduction

3-Methacryloxyproyltrimethoxysilane (MPS) is the commonly used clinical commercial silane primers (1). There are two types of silane, one is a pre-hydrolyzed one-bottle system and the other one is a two-bottle system. Pre-hydrolyzed silane results in a self-condensation reaction over time, and thus cannot be used for the clinical purpose. This also results in a shorter shelf life compared to the two-bottled one. The two-bottle system contains un-hydrolyzed silane in ethanol in one bottle and an aqueous acetic acid solution in the other. Keeping them in separate bottles increases the shelf life of silane (2). The combined use of silane with a resin adhesive improves the bond strength of the composite to the glass ceramic (3).

Condensation reaction, referred to as dehydration synthesis, is a chemical reaction in which two molecules combine to form a larger molecule with the loss of a small molecule. The most common small molecule is water. The condensation reaction of silane also produces a by-product, which is water. The larger molecule formed as a result of this condensation reaction loses the water molecule and has a greater density than the reactants (4). The condensation reaction between two hydroxyl groups results in a covalent bond (chemical bond), where the silane molecule firmly attached to the porcelain surface. A by-product is the loss of a water molecule (5).

Le Chatelier's principle, also called "The Equilibrium Law", stated that "When a system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to counteract the effect of the applied change and a new equilibrium is established" (6). The condensation reaction of silane generates water, and this water changes the equilibrium in the system. The water must be eliminated in order to promote condensation reaction. This is the reason why warm air-drying is recommended after you apply silane (7).

The chemical reaction between silane and a silica-based porcelain surface produces water as a by-product. This chemical reaction is called condensation reaction, and in order for this reaction to be continuous, the resulting by-product of water must be continuously removed. Equilibrium, according to "Le Chatelier's" principle, can be achieved by water removal for further chemical reaction. The dental adhesive has to contain a hydrophobic resin monomer in order to increase bond strength and prevent any hydrolytic degradation. If a hydrophobic resin monomer and silane are combined into a one-bottle adhesive system, then the hydrophobic resin monomer disturbs the process of by-product elimination, which is water evaporation. The trend these days is to use a hydrophobic resin with higher hydrophobic properties in order to increase the longevity of the bonding layer. Recently marketed Single Bond Universal adhesive from 3M ESPE (3M ESPE, St. Paul, MN, USA) is one adhesive system which contains this type of hydrophobic monomer, MDP.

There are several adhesives which include silane in the same bottle such as Single Bond Universal mentioned above. It is convenient to use the same bottle for the adhesive as well as to treat the surface of the silica-based ceramic. However, it is possible that the effectiveness of the resin and silane may be reduced because of the change in properties when they are combined in one bottle.

Therefore, the null hypothesis of this study was that there would be no significant difference between a) the adhesive is applied after silane group and 2) silane and adhesive combined in one bottle group on silica-based porcelain in terms of surface hydrophobicity and shear bond strength.

Materials and Methods

1. Material

A silane monomer, MPS, which is the active ingredient for most dental silane primers, was added into a universal adhesive (All-Bond Universal, ABU, Bisco, Schaumburg, IL, USA), resulting in an experimental silane-containing adhesive (Sil-ABU) which contains 4 wt% of the silane monomer.

The materials used in this study are as follows: ABU only, silane mixed with ABU (Sil-ABU), porcelain primer (which is a regular silane primer) only, and Scotch Bond Universal (SBU, 3M ESPE, St. Paul, MN, USA) which is a commercial silane-containing universal adhesive. IPS e-max press (Ivoclar Vivadent, Schaan, Liechtenstein), a lithium disilicate, was used as the silica-based ceramic. In terms of shade matching, IPS e-max press has more aesthetic characteristics compared to any other CAD-CAM ceramic block. Duolink resin cement (Bisco, Schaumburg, IL, USA) was used as a composite applied to the surface to test for shear bond strength (Table 1).

2. Contact angle

For the contact angle test, lithium disilicate, IPS e.max, disc was etched with hydrofluoric acid (Bisco Porcelain Etchant, 4% HF, Lot # 1200010466, Bisco, Schaumburg, IL, USA) for 25 sec., rinsed with water and dried (Group 1). The etched lithium disilicate disc was then treated with ABU (Group 2), ABU and Silane (Group 3), SBU (Group 4) or porcelain primer (Group 5) (Table 2). All samples were then left undisturbed for 5 min and cleaned by ultrasonication for 2 min in ethanol. Samples were then dried and contact angles were measured with contact angle meter (NRL-CA Goniometer, Rame-Hart Inc, Randolph, NJ, USA).

Table 1. Materials used in this study

Materials	Ingredient	Manufacturer
All Bond Universal (ABU)	Bis-GMA, MDP	Bisco
ABU & Silane (Sil-ABU)	Bis-GMA, MDP, Silane	Experimental mixture
Scotch Bond Universal (SBU)	Bis-GMA, MDP, Vitrebond copolymer, Silane	3M ESPE
Porcelain primer	Silane	Bisco
IPS e.max	Lithium disilicate	Ivoclar Vivadent
Duolink	Bis-GMA, Glass fiber	Bisco

Table 2. Control and experimental group for measuring contact angle

Group	Procedure	Remarks
1	HF etch – rinse – dry	Control
2	HF etch – rinse – dry – ABU	Experimental Group
3	HF etch – rinse – dry – Sil-ABU	Experimental Group
4	HF etch – rinse – dry – SBU	Experimental Group
5	HF etch – rinse – dry – porcelain primer	Experimental Group

3. Shear bond strength

Lithium disilicate (IPS e.max, Ivoclar Vivadent) was wet-polished with 320-grit SiC sandpaper, rinsed with water and dried. The dual cured resin cement Duolink (Bisco; Lot #1300004782), was applied on polished lithium disilicate disc followed by light curing with 40 sec/500 mW/cm^2 (Group 1). The polished lithium disilicate was treated with either ABU (Group 2), ABU-Sil (Group 3) or SBU (Group 4) (Table 3). Samples were then left undisturbed (1 min), and light light-cured for 10 sec. Polished disc that were left undisturbed for 1 min after treated with porcelain primer was applied with ABU separately, and light cured for 10 sec (Group 5) (Table 3). Duolink was used to fabricate a composite post (bonding area = 4.5 mm^2). Duolink was light cured for 40 sec using light curing unit at energy density of 500 mW/cm^2 from the top. The polymerized specimens were stored in de-ionized water for 24 hr at 37 ℃, then tested until failure using universal testing machine (Instron 4466) at a cross head speed of 1 mm/min.

4. Statistical analysis

The statistical significances of the resulting data were analyzed using one-way ANOVA. The statistical significance was accepted at confidence level of 95 % ($p<0.05$) by Tukey's test for a multiple comparison procedure. The SPSS PASW 18.0 program (SPSS Inc., IBM, Amonk, NY, USA) was used for the statistical analysis.

Results

1. Contact angle

The results of the contact angle test showed that the experimental groups (Groups 2~4) and the control group (Group 1) were not statistically different ($p>0.05$), except for Group 5. Group 5, the group that used silane only with porcelain primer, showed the highest contact angle compared to any other groups ($p<0.05$) (Figure 1).

2. Shear bond strength

In the shear bond strength test, all experimental groups (Group 2~5) were statistically different from the control group (Group 1) ($p<0.05$) (Figure 2). However, there was a significant difference between Group 5 and the other experimental groups (Groups 2~4) and the control group (Group 1) ($p<0.05$).

Discussion

Silica-based ceramics, such as feldspathic porcelain and glass ceramics, are frequently used to veneer metal frameworks or high-strength ceramic coping for all-ceramic restorations. Availability of improved dental ceramic materials such as lithium disilicate, alumina, and zirconia as core materials has to led to a widespread

Table 3. Control and experimental group for shear bond strength test

Group	Procedure	Remark
1	Polish - no primer - Duolink	Control
2	Polish - ABU - Duolink	Experimental Group
3	Polish - Sil & ABU - Duolink	Experimental Group
4	Polish - SBU - Duolink	Experimental Group
5	Polish - silane - ABU - Duolink	Experimental Group

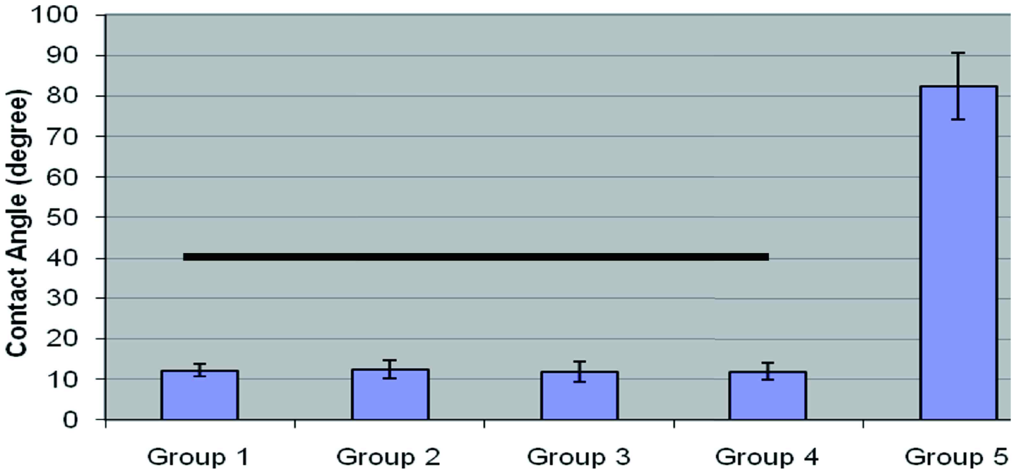

Figure 1. Contact angle on primed etched lithium disilicate. Horizontal bar means that there are no significantly different ($p>0.05$).

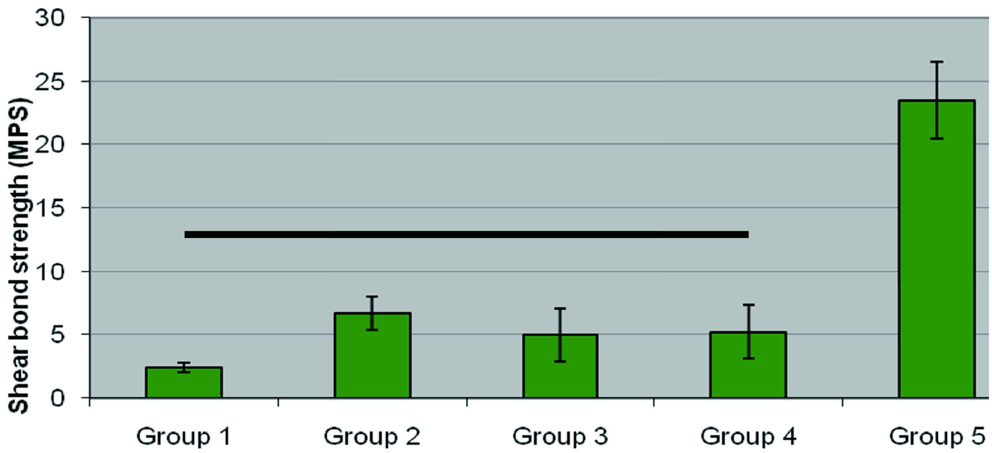

Figure 2. Shear bond strength on polished lithium disilicate. Horizontal bar means that there are no significantly different ($p>0.05$).

use of all-ceramic restorations over the past decade (8).

Due to the development of new restorative material in today's esthetic dentistry, there emerges a clinical demand for the development of multi-purpose primers or adhesives that can deliver strong and durable adhesion to surfaces such as dental hard tissues, dental ceramics, dental precious metal alloys and dental non-precious metals (9).

Universal bonding adhesives are the most recent bonding agent in dental area. Universal bonding adhesive refers to a dental adhesive that can be used for both total etch and self etch techniques. These universal bonding adhesives are not only technically universal, but also functionally universal. They can be used as a multi-purpose surface treatment for silica-based ceramic, zirconia and dentin. Before this generation of one-bottle adhesives, MDP was and still is used separately to chemically treat the surface of zirconia (10) and silane was and still is commonly used for treatment of silica-based ceramic surfaces. Now, the so-called universal bonding adhesives incorporate these ingredients into one bottle to treat different surfaces as well as to act as an adhesive.

Even though mechanical strength is an important factor that controls the clinical success of dental restoration (11), the surfaces of the specimens were polished in order to eliminate any bias from micro mechanical retention due to an uneven surface. Two major factors of porcelain bonding strength are how to treat the porcelain surface both physically and chemically. Hydrofluoric acid etching helps to expand the surface (12) and enhances bonding strength(13). Silane primer increases chemical bonding strength through condensation reaction with the ceramic surface. Thus, in this study, all of the surfaces of the specimens were polished by sand paper to evaluate only the chemical function of silane.

Adhesion requires intimate contact of the materials to be joined. Surface has to be more hydrophobic for better adhesion, such as universal adhesive which hydrophobic resin as a ingredient (14). Most manufacturers use Bis GMA or MDP as the hydrophobic monomer in their universal adhesives. Some of these adhesives combine both silane and a hydrophobic functional monomer, such as BisGMA or MDP.

However, this hydrophobic resin interferes with the condensation reaction of the pre-hydrolyzed silane inside the one-bottle universal adhesives (15). This resin interferes with the evaporation process of the water by-product of the condensation reaction and prevents equilibrium for further chemical reaction. There is a study that shows that warm air drying significantly increases the coupling potential of silane-based primers used as intermediate agents (7).

The result of this study shows that combining silane with ABU or SBU produces a relatively low contact angle. This means the surface is still hydrophilic and resin-unfriendly after applying the material. Silane does not work on a porcelain surface if it is mixed with a hydrophobic resin monomer. Applying silane to the porcelain surface generates water as a by-product. Water must be removed in order to accelerate the chemical reaction, but due to the hydrophobic resin inside the one bottle adhesive, water will be captured inside the resin matrix, and the chemical reaction cannot continue.

In terms of shear bond strengths, silane mixed with a hydrophobic resin monomer (Bis-GMA or MDP) showed relatively lower data than applying only silane. Silane in a hydrophobic resin monomer cannot effectively react with the porcelain surface, and results in a relatively low contact angle and poor bond strength.

Combining silane with the hydrophobic resin monomer hinders the silane from properly treating the porcelain surface. This is proven by the results of the contact angle tests and shear bond strength tests comparing one-bottle adhesives that include silane to using silane separately from the adhesive.

Conclusions

Silane should be used separately from a hydrophobic resin monomer in order to maximize its porcelain surface treatment function. Using silane separately and using silane incorporated into the universal adhesive (contains hydrophobic resin) do not perform equally on silica-based ceramic.

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Original Article

Effect of silane incorporated adhesive or adhesive using separate silane on bonding of silica-based ceramics

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The purpose of this study was to evaluate the effectiveness of silane on the surface treatment of silica-based ceramic when silane is incorporated into the universal adhesive versus using silane separately from the adhesive. The materials used in this study are as follows: 1) All-Bond Universal, 2) Silane mixed with All-Bond Universal, 3) Porcelain primer (as a regular silane primer), and 4) Scoth Bond Universal (which is a commercial silane-containing universal adhesive). IPS e-Max press, a lithium disilicate, was used as the silica-based ceramic. Contact angle test was measured to evaluate hydrophobicity on a silica-based ceramic surface. Shear bond strength was tested by universal testing machine. The surfaces of the specimen were polished in order to eliminate any bias from micro mechanical retention due to an uneven surface. The results indicated that only silane applied to the silica based ceramic surface resulted in highest contact angle and shear bond strength. Using silane separately and using silane incorporated into the universal adhesive (contains hydrophobic resin) resulted in different performance on silica-based ceramic. Therefore, it was concluded that the silane should be used separately from a hydrophobic resin monomer in order to maximize its porcelain surface treatment function.

Keywords : Silane, Universal adhesive, One bottle adhesive, Surface treatment, Silica based ceramic, Lithium disilicate