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Interfacial Characteristics and Bond Durability of Universal Adhesive to Various Substrates

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Clinical Relevance

Clinicians should follow the procedures associated with universal adhesives to modify the interfacial characteristics carefully and pay attention to the factors that contribute to the bond durability of universal adhesives with various substrates; in particular, clinicians should be aware of their chemical bonding potential.

SUMMARY

Objective: This study investigated the interfacial characteristics and bond durability of universal adhesives to various substrates.

Methods and Materials: Two universal adhesives were used: 1) Scotchbond Universal and 2) G-Premio Bond. The substrates used were bovine enamel and dentin with or without phosphoric acid etching, resin composite, lithium disilicate and leucite-reinforced glass ceramics, zirconia, and metal alloys. The surface free energy and the parameters of various substrates and of substrates treated by adhesive after light irradiation were determined by measuring the contact angles of three test liquids. Resin composite was bonded to the various substrates to determine shear bond strength after 24 hours water storage and 10,000 thermal cycles. A one-way analysis of variance (ANOVA) and the Tukey post hoc test were used for the surface free energy data, and a two-way ANOVA and the Tukey post hoc test were used for analysis of shear bond strength data (α=0.05).

Results: The interfacial characteristics of the various substrates show significant differences depending on the type of substrate, but the interfacial characteristics of substrate treated by adhesive after light irradiation did not show any significant differences regardless of the substrate used. The bond durability of two universal adhesives to various substrates dif-

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fers depending on the type of substrate and the adhesive.

Conclusions: The results of this study suggest that universal adhesives modify the interfacial characteristics of a wide range of substrates and create a consistent surface, but the bond durability of universal adhesive to various substrates differs depending on the type of substrate and the adhesive.

INTRODUCTION

The introduction of new-generation adhesive systems has aimed at reducing technique sensitivity and the number of clinical steps required for adhesion.[1] There has been a trend toward the use of less time-consuming options, such as single-step self-etch adhesives.[2] Continuing this trend, universal adhesives have recently been introduced to the profession.[3] Universal adhesives are designed to bond to tooth structures via the total-, self-, or selective-etch technique.[4] In addition, some universal adhesives are also capable of bonding to various substrates, including resin composite, glass ceramics, zirconia, and metal alloys, with no need for additional primers.[5] The versatility offered by universal adhesives provides for a new, simplified approach to bonding between resins and various substrates.[6] However, because of the recent introduction of universal adhesives, little information is currently available about the bond durability of universal adhesives to various substrates.

The surface modification of various substrates by universal adhesive is important for bonding with resin composite because the surface properties of restorative materials differ.[7] Previous studies[8,9] have shown that the surface modification and coating capacity of adhesives can be analyzed on the fundamentals of interface science. The interfacial characteristics of substrates treated by adhesives, including wetting ability, polarization, and hydrophilicity, may be measured in terms of the surface free energy.[10,11] Adhesion requires intimate contact at both the substrate-adhesive and adhesive-restorative interfaces in order to form tight and durable connections.[12] Since the interfacial characteristics of the substrates that compose the adhesive interface are different depending on their compositions, understanding of the interfacial characteristics of substrates and substrate treated by adhesive is essential to understanding and promoting intimate contact among substrate, adhesive, and restorative materials.[13] Thus, analysis of the interfacial characteristics of a wide range of substrates treated by universal adhesives may provide novel insight into the basis of the bond durability of universal adhesive with various substrates.

Evaluation of bond durability is important, since the stability of the bond between the adhesive and substrates is related to the long-term clinical success of restorations.[14] Although the most reliable conclusions about the performance of adhesives in the oral environment are derived from long-term clinical trials, long-term aqueous storage of the bonded specimen or subjecting it to thermal cycling may provide valuable information about bond durability.[15] A thermal cycling test is the process of subjecting bonded specimens to cyclic temperature changes through water immersion in order to simulate intraoral conditions.[16] A previous study[17] established that 10,000 thermal cycles (TC) correspond to one year of clinical function of restorations, and this estimate is based on the hypothesis that such cycles might occur 20 to 50 times a day. Universal adhesives differ from the current self-etch adhesives in the incorporation of monomers that are capable of modifying surfaces and producing chemical bonding to the various substrates.[18] A commonly used monomer is 10-methacryloyloxydecyl dihydrogen phosphate (MDP), which helps bond not only tooth substrates but also metal oxides,[5,7] and some universal adhesives include silane to bond with glass ceramics[6] or sulfur-containing monomers to improve bonding with noble metals.[19] It is postulated that this incorporation may increase the bond durability of universal adhesives to various substrates.

The purpose of this laboratory study was to investigate the influence of universal adhesive on the interfacial characteristics of various substrates by measuring changes in surface free energy and the parameters. In addition, the bond durability of universal adhesives to various substrates was determined to assess the effects of the surface modifications. The null hypotheses to be tested were the following: 1) The interfacial characteristics of various substrates would not be influenced by treatment with universal adhesives; and 2) There would not be differences in the bond durability of universal adhesives to various substrates.

METHODS AND MATERIALS

Adhesive Systems

Two universal adhesives were used in this laboratory investigation: 1) Scotchbond Universal (SU; 3M ESPE, St Paul, MN, USA) and 2) G-Premio Bond (GB; GC, Tokyo, Japan). The adhesives and associ-

Table 1: *Materials Used in This Study*

Materials (Lot No.)	Type of Material (Code)	Main Components	Manufacturer
Scotchbond Universal (566724)	Universal adhesive (SU)	MDP, Bis-GMA, HEMA, Vitrebond copolymer, polyethylene glycol, water, initiator, colloidal silica, silane	3M ESPE, St Paul, MN, USA
G-Premio Bond (541424)	Universal adhesive (GB)	MDP, 4-MET, MEPS, methacrylate monomer, acetone, water, initiator, silica	GC, Tokyo, Japan
Clearfil AP-X (1312131)	Resin composite (RC)	Bis-GMA, TEGDMA, silanated barium filler, silanated colloidal silica, DL-camphorquinone, catalysts, accelerators, pigments, others	Kuraray Noritake Dental, Tokyo, Japan
IPS e.max CAD (P23546)	Lithium disilicate glass ceramic (LD)	SiO_2, Li_2O, K_2O, P_2O_5, ZrO_2, ZnO, other oxides, pigments	Ivoclar Vivadent, Schaan, Lichtenstein
IPS empress CAD (T43858)	Leucite-reinforced glass ceramic (LR)	SiO_2, Al_2O_3, K_2O, Na_2O, other oxides, pigments	Ivoclar Vivadent
IPS e.max ZirCAD (T22482)	Zirconia (ZR)	SiO_2, Al_2O_3, K_2O, Na_2O, other oxides, pigments	Ivoclar Vivadent
Casting Gold M.C. type III (1011741)	Type III gold alloy (GA)	Au, Cu, Ag, Pd, others	GC
Castwell M.C. 12 (1312041)	Au-Ag-Pd alloy (AP)	Au, Ag, Pd, Cu, Au, others	GC
Ultra-Etch (N017)	Phosphoric acid pre-etching agent	35% Phosphoric acid	Ultradent Products, South Jordan, UT, USA
Ceramic Primer II (1402101)	Silane coupling agent	Silane, MDP, ethanol	GC

Abbreviations: Bis-GMA, bisphenol A glycidyl methacrylate; 4-MET, 4-methacryloyloxyethyl trimellitate; HEMA, 2-hydroxyethyl methacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; MEPS, methacryloyloxyalkyl thiophosphate methylmethacrylate; TEGDMA, triethylene glycol dimethacrylate.

ated lot numbers and components are shown in Table 1. Ultra-Etch (Ultradent Products, South Jordan, UT, USA) was used as a 35% phosphoric acid pre-etching agent. According to the manufacturers' instructions, SU does not require a silane coupling treatment to glass ceramics, but GB does require a silane coupling treatment (Ceramic Primer II, GC) to bond adhesive to glass ceramics.

Bonding Substrates

The substrates for bonding with universal adhesives (Table 1) were as follows: 1) bovine enamel and dentin, 2) resin composite: Clearfil AP-X (RC; Kuraray Noritake Dental, Tokyo, Japan), 3) lithium disilicate glass ceramic: IPS e.max CAD (LD; Ivoclar Vivadent, Schaan, Liechtenstein), 4) leucite-reinforced glass ceramic: IPS empress CAD (LR; Ivoclar Vivadent), 5) zirconia: IPS e.max ZirCAD (ZR; Ivoclar Vivadent), and 6) metal alloys: Casting Gold M.C. type Ш (GA, GC) and Castwell M.C. 12 (AP, GC).

Specimen Preparation

Mandibular incisors extracted from two- to three-year-old cattle and stored frozen (–20°C) for up to two weeks were used. After removing the roots using a water-cooled precision diamond saw (IsoMet 1000, Buehler, Lake Bluff, IL, USA), the pulps were removed, and the pulp chamber of each tooth was filled with cotton to prevent penetration of the embedding media. After ultrasonic cleaning for 30 seconds in distilled water to remove excess debris, the surfaces were washed and dried with oil-free compressed air. The labial surfaces were ground with wet #180-grit silicon carbide (SiC) paper to create flat enamel and dentin surfaces.

LD, LR, and ZR plates were cut from CAD/CAM ceramic blocks using a water-cooled precision diamond saw to produce specimens that were $10 \times 10 \times 2$ mm thick. All of the ceramic plates were crystallized in a ceramic furnace (Programat S1, Ivoclar Vivadent) according to the manufacturers' instructions.

Metal disks, 10 mm in diameter and 2 mm in thickness, with an attached loop were fabricated with the flat surface of each disk perpendicular to the loop and cast in GA and AP according to the manufacturers' instructions.

Each specimen was then mounted in self-curing acrylic resin (Tray Resin II, Shofu, Kyoto, Japan) to expose the flattened area and placed under tap water to reduce the temperature rise caused by the exothermic polymerization reaction of the acrylic resin. The surfaces of various substrates were ground with #320-, #600-, #1200-, and #2000-grit

SiC paper. These surfaces were then washed and dried with oil-free compressed air. Enamel and dentin with phosphoric acid pre-etching (phosphoric acid applied for 15 seconds prior to application of the adhesive) or without phosphoric acid pre-etching (phosphoric acid was not applied) were also prepared.

Surface Free Energy Measurements

After preparation, the samples for surface free energy measurement were divided into two sets. One set of substrate samples was left untreated after the specimen preparation. The adhesives were applied to each of the various surfaces according to the manufacturers' instructions in the other set, and this set was light irradiated for 10 seconds with a quartz-tungsten halogen unit (Optilux 501, Kerr, Orange, USA). The power density (above 600 mW/cm^2) of the quartz-tungsten halogen unit was checked using a dental radiometer (model 100, Kerr) before preparing the specimens. Contact angles were measured to investigate the surface free energy characteristics of the various substrates and of the substrate treated by adhesive after light irradiation.

The surface free energy characteristics of the various substrates and of substrates treated by adhesive after light irradiation were determined by measuring the contact angles formed with the surface by three test liquids—bromonaphthalene, diiodomethane, and distilled water—each of which has known surface free energy parameters. For each test liquid, the equilibrium contact angle (θ) was measured by the sessile drop method under ambient conditions of 23°C ± 2°C and 50% ± 10% relative humidity using a contact angle measurement apparatus (DM 500, Kyowa Interface Science, Saitama, Japan) for 10 specimens per group. The apparatus was fitted with a charge-coupled device camera to enable automatic measurement. A standardized 1-μL drop of each test liquid was placed on the cured adhesive and uncured resin composite surfaces, and a profile image was captured after 500 ms using the apparatus. Contact angles were then calculated by the θ/2 method using the built-in interface measurement and analysis system (FAMAS, Kyowa Interface Science).

The surface free energy parameters of the solids were then calculated based on the fundamental concepts of wetting. The Young-Dupré equation describes the work of adhesion (W) between a solid (S) and a liquid (L) in contact as follows:

$$W_{SL} = \gamma_L + \gamma_S - \gamma_{SL} = \gamma_L(1 + \cos\theta).$$

Here, γ_{SL} is the interfacial free energy between the solid and liquid, γ_L is the SFE of the liquid, and γ_S is the surface free energy of the solid. By extending the Fowkes equation, as developed by Kitazawa-Hata, γ_{SL} can be expressed as follows:

$$\gamma_{SL} = \gamma_L + \gamma_S - 2(\gamma_L^d\gamma_S^d)^{1/2} - 2(\gamma_L^p\gamma_S^p)^{1/2} - 2(\gamma_L^h\gamma_S^h)^{1/2}$$

$$\gamma_{\mathrm{L}} = \gamma_L^e + \gamma_L^p + \gamma_L^h, \gamma_{\mathrm{S}} = \gamma_S^d + \gamma_S^p + \gamma_S^h,$$

where γ_L^d, γ_L^p, and γ_L^h are components of the surface free energy arising from the dispersion force, the polar force, and the hydrogen bonding force, respectively. Surface free energy values were determined for the three test liquids, and the surface free energy parameters were calculated based on these equations using the built-in software.

Shear Bond Strength (SBS) Test

The various substrates were prepared as described above. An Ultradent Bonding Assembly (Ultradent Products) was used for determining SBS. The adhesives were applied to the various substrates according to the manufacturers' instructions. Following the application of the adhesive to the bonding sites, bonded resin composite cylinders were formed on the adherends by clamping plastic molds (2.4 mm in internal diameter, approximately 2.5 mm in height) in the fixture against the various substrates. The resin composite (Clearfil AP-X, Kuraray Noritake Dental) was inserted all at once into the mold and then light irradiated for 40 seconds. The plastic mold was removed, and the finished specimens were transferred to distilled water and stored at 37°C for 24 hours, after which they were randomly allocated to two groups (n=25 per group) for thermal cycling: 1) no thermal cycling (24 h group); 2) 10,000 TC between 5°C and 55°C (TC group). Thermal cycling was conducted using a thermocycling machine (Thermal Shock Tester TTS-1 LM, Thomas Kagaku, Tokyo, Japan). Each cycle consisted of water-bath incubation for 30 seconds, with a transfer time of five seconds.

SBS measurements were performed using a universal testing machine (Type 5500R, Instron Worldwide Headquarters, Norwood, MA, USA) equipped with an Ultradent shearing fixture at a crosshead speed of 1.0 mm/min. An Ultradent shear bond test with a semicircular blade of 2.4-mm diameter was used for SBS measurement. The SBS values (MPa) were calculated from the peak load at failure divided by the bonding area. After testing,

Table 2: *Surface Free Energy and their Parameters of Various Substrates*[a]

Substrate	γ_S	γ_S^d	γ_S^p	γ_S^h
Enamel (etching)	71.6 (2.4) A	41.1 (0.7) A	11.3 (1.5) A	19.2 (2.2) A
Enamel (no etching)	55.9 (3.5) B	40.6 (0.7) A	3.8 (1.5) B	11.5 (2.4) B
Dentin (etching)	62.3 (3.4) C	40.8 (0.5) A	4.3 (1.3) B	17.1 (3.0) A
Dentin (no etching)	67.6 (3.4) D	41.0 (0.6) A	6.3 (1.2) C	20.3 (3.3) A
Resin composite	54.0 (2.4) B	40.4 (0.3) A	5.6 (1.2) C	8.0 (1.2) C
Lithium disilicate	69.0 (2.4) D	40.8 (0.6) A	9.1 (1.2) D	19.1 (3.4) A
Leucite glass ceramic	70.2 (2.1) AD	41.1 (0.6) A	9.6 (1.2) D	19.5 (2.4) A
Zirconia	67.9 (2.4) D	41.0 (0.6) A	9.0 (1.5) D	17.9 (2.3) A
Type III gold alloy	64.2 (2.1) C	40.9 (0.6) A	7.1 (1.0) C	16.2 (1.4) D
Au-Ag-Pd alloy	62.0 (2.9) C	40.7 (0.3) A	6.5 (1.2) C	14.9 (1.2) E

Abbreviation: Au-Ag-Pd alloy, gold-silver-palladium alloy.
[a] *Unit: mN/m; values in parenthesis are standard deviations (n=10). Same letter in vertical columns indicates no significant difference (p>0.05).*

the specimens were examined under an optical microscope (SZH-131, Olympus, Tokyo, Japan) at a magnification of 10× to assess the type of the bond failure. The proportions of the resin composite surface with adherent and visible remnants were estimated and used to classify the failure as follows: 1) adhesive failure; 2) cohesive failure in the substrate, 3) cohesive failure in the resin composite; and 4) mixed failure (combination of adhesive and cohesive failure).

Statistical Analysis

The surface free energy and SBS data obtained were analyzed using a commercial statistical software package (SPSS Statistics Base, IBM, Armonk, NY, USA). A one-way analysis of variance (ANOVA) and Tukey post hoc test were used for surface free energy data, and a two-way ANOVA and Tukey post hoc test were used for analysis of SBS data, with a significance level of 0.05.

RESULTS

Surface free energy Measurement of Various Substrates and Substrates Treated by Adhesive

The results for the surface free energy and their parameters of the various substrates are shown in Table 2. The surface free energy and their parameters of the various substrates show significant differences depending on the type of substrate used. The influence of the treatment with universal adhesives of the various substrates on surface free energy and their parameters is shown in Table 3. Surface free energy and their parameters of substrates treated by adhesive after light irradiation did not show any significant differences among the substrates, and the interfacial characteristics of substrates treated by adhesive after light irradiation were closer to those of untreated RC than those of various substrates.

SBS Tests of Universal Adhesives to Various Substrates

The influence of type of substrate on the SBS of universal adhesives 24 h and TC groups is shown in Figures 1 and 2. The two-way ANOVA revealed that the type of substrate and adhesive used did have a significant influence on SBS 24 h and TC groups. In addition, there was a significant effect for the interaction of the type of substrate and adhesive for SBS 24 h and TC groups. The failure modes of debonded specimens after SBS tests are shown in Table 4. Failure type was not associated with SBS, and the predominant type of failure seen was adhesive failure.

SBS of Universal Adhesives to Enamel

The SBSs of universal adhesives to enamel with and without phosphoric acid pre-etching 24 h and TC groups ranged from 25.7 ± 3.6 to 36.7 ± 4.4 MPa. The SBSs of universal adhesives to enamel with phosphoric acid pre-etching 24 h and TC groups were significantly higher than those without phosphoric acid pre-etching and did not depend on the type of adhesive used.

SBS of Universal Adhesives to Dentin

The SBSs of universal adhesives to dentin with and without phosphoric acid pre-etching 24 h and TC groups ranged from 26.6 ± 3.2 to 31.2 ± 4.2 MPa. The SBSs of universal adhesives to dentin with and without phosphoric acid pre-etching were similar and did not depend on the type of adhesive. In addition, the SBSs to dentin of TC group were higher

Table 3: *Influence of the Treatment with Universal Adhesives of the Various Substrates*[a]

Substrate	Adhesive	γ_S	γ_S^d	γ_S^p	γ_S^h
Enamel (etching)	SU	59.1 (2.2) A	40.6 (0.2) A	7.1 (0.6) A	11.4 (1.0) A
	GB	58.8 (1.9) A	40.3 (0.3) A	7.0 (0.5) A	11.5 (1.2) A
Enamel (no etching)	SU	57.8 (1.8) A	40.5 (0.8) A	6.1 (0.9) A	11.2 (1.9) A
	GB	57.0 (1.7) A	40.4 (0.7) A	5.8 (0.5) A	10.8 (1.8) A
Dentin (etching)	SU	58.8 (1.8) A	40.5 (0.7) A	6.8 (0.9) A	11.5 (1.8) A
	GB	58.3 (1.5) A	40.3 (0.4) A	6.4 (0.5) A	11.6 (1.1) A
Dentin (no etching)	SU	57.4 (1.8) A	40.5 (0.8) A	6.0 (0.9) A	10.9 (1.4) A
	GB	57.2 (1.8) A	40.4 (0.7) A	5.9 (0.5) A	10.9 (1.6) A
Resin composite	SU	59.1 (2.1) A	40.5 (0.3) A	7.0 (0.8) A	11.6 (1.1) A
	GB	58.6 (2.0) A	40.4 (0.3) A	7.0 (0.7) A	11.3 (1.2) A
Lithium disilicate	SU	57.6 (1.8) A	40.4 (0.8) A	6.1 (0.9) A	11.1 (1.2) A
	GB	57.3 (1.7) A	40.4 (0.6) A	6.1 (0.9) A	10.8 (1.2) A
Leucite glass ceramic	SU	57.9 (1.7) A	40.4 (0.8) A	6.2 (0.9) A	11.3 (1.8) A
	GB	57.2 (1.7) A	40.4 (0.7) A	6.0 (0.7) A	10.8 (1.6) A
Zirconia	SU	58.5 (1.8) A	40.5 (0.5) A	6.4 (0.9) A	11.6 (1.9) A
	GB	57.2 (1.3) A	40.3 (0.5) A	6.1 (0.7) A	10.8 (1.5) A
Type III gold alloy	SU	58.2 (1.8) A	40.5 (0.5) A	6.4 (0.9) A	11.3 (1.5) A
	GB	57.5 (1.8) A	40.3 (0.5) A	6.0 (0.7) A	11.2 (1.3) A
Au-Ag-Pd alloy	SU	58.3 (1.8) A	40.5 (0.4) A	6.3 (0.9) A	11.5 (1.5) A
	GB	57.4 (1.5) A	40.3 (0.4) A	6.1 (0.7) A	11.0 (1.4) A

Abbreviations: Au-Ag-Pd alloy, gold, silver, palladium alloy; GB, G-Premio Bond; SU, Scotchbond Universal.
[a] *Unit: mN/m; values in parenthesis are standard deviations (n==10). Same letter in vertical columns indicates no significant difference ($p>0.05$).*

than those of 24 h group, regardless of the presence or absence of phosphoric acid pre-etching.

SBS of Universal Adhesives to Resin Composite

The SBSs of universal adhesive to RC 24 h and TC groups ranged from 30.4 ± 3.9 to 34.5 ± 2.6 MPa and also did not show any significant differences depending on the type of adhesive used.

SBS of Universal Adhesives to Glass Ceramics

The SBSs of universal adhesives to LD and LR ranged from 2.9 ± 1.9 to 13.9 ± 4.1 MPa, and the SBSs of GP to LD and LR 24 h and TC groups were higher than those of SU.

SBS of Universal Adhesives to Zirconia

The SBSs of universal adhesives to ZR 24 h and TC groups ranged from 16.1 ± 3.1 to 28.8 ± 3.7 MPa. Although the SBSs of SU to ZR of 24 h group were significantly higher than those of GB, SU showed a significantly lower SBS to ZR of TC group than did GB.

SBS of Universal Adhesives to Metal Alloys

The SBS of universal adhesives to GA and AP ranged from 8.2 ± 3.0 to 18.8 ± 3.4 MPa. The SBSs to GA and AP of GB of 24 h and TC groups were significantly higher than those of SU.

DISCUSSION

The present study indicated that the surface free energy (γ_S,) and their parameters (γ_S^p and γ_S^h) of the various substrates was material dependent, but there were no significant differences in γ_S^d values between the types of substrates. It has been reported that the γ_S^d values of oxidized surfaces measured using this method are generally approximately 40 mN/m.[20,21] On the other hand, the γ_S^p value, which reflects polar interactions, and the γ_S^h value, which relates to the water and hydroxyl components, together measure hydrophilic interactions.[9] Therefore, it may be assumed that the interfacial characteristics of various substrates were influenced by the hydrophilicity of the tested surface, which depends on the different compositions of the various substrates.

The surface free energy and their parameters of substrates treated by adhesive after light irradiation did not show any significant differences among the substrates. After treatment with the current single-step adhesives, the substrates are covered with adhesive, which forms a thin layer (less than 10

Fig 1

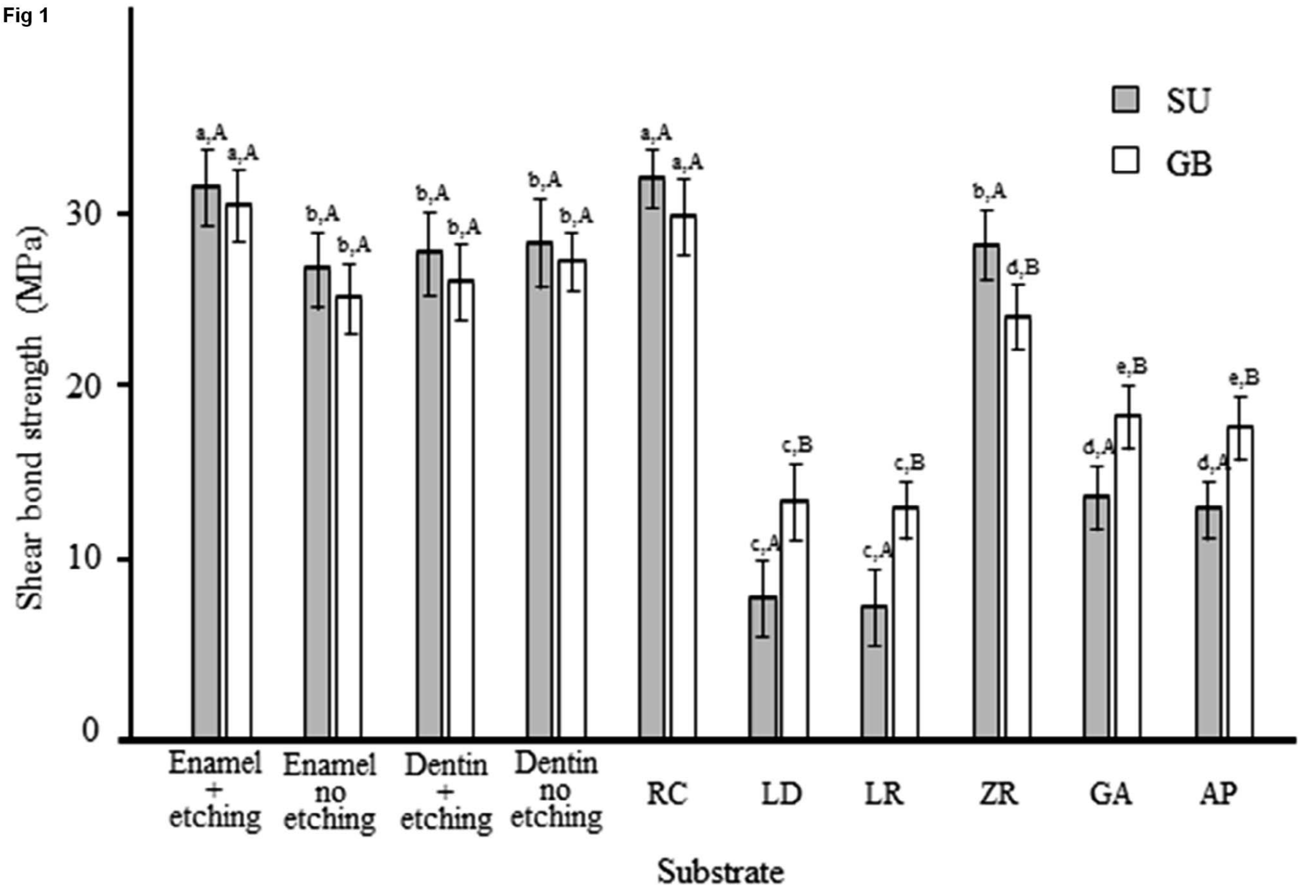

Figure 1. *Influence of type of substrate on the shear bond strength (MPa) of universal adhesives after 24 hours. The same lowercase letter indicates no significant differences between types of substrate. The same capital letter indicates no significant differences between adhesives. Abbreviations: SU, Scotchbond Universal; GB, G-Premio Bond; RC, resin composite; LD, lithium disilicate; LR, leucite reinforced; ZR, zirconia; GA, gold alloy, AP, gold-palladium.*

μm).[22] Although this raises a concern that the substrates might influence the surface properties or, as a result of incomplete wetting, might still be exposed in some locations, these results indicate that the universal adhesive achieves a consistent surface on a wide range of substrates.

The interfacial characteristics of substrates treated by adhesive after light irradiation were closer to those of untreated RC than those of various substrates. Optimal wettability is important to enable materials to spread across the entire surface and to establish adhesion.[23,24] Although the surface free energy of the adhesive surface must be maximized, the maximum bond strength is assumed to arise when the surface free energy parameters of the resin composites are close to those of the adhesive treated surface.[8] Therefore, the interfacial characteristics of substrate treated by adhesive after light irradiation are similar to those of resin composite, resulting in effective adhesion sites that have a proper balance between the surface free energy parameters of adhesive coated surfaces and resin composite. These results indicate that universal adhesives modify the interfacial characteristics of a wide range of substrates and coat them to create a consistent surface. Thus, in the clinic, it is possible to use these adhesives with a wide range of substrates, as long as the procedures are followed carefully. Overall, the results of this study require rejection of the null hypothesis that the interfacial characteristics of the various substrates would not be influenced by treatment with universal adhesives.

Although the modifying and coating ability of universal adhesives with substrates might improve their bond durability to various substrates, in the present study bond durability of universal adhesive to various substrates was different depending on the type of substrate and the adhesive. One of the key

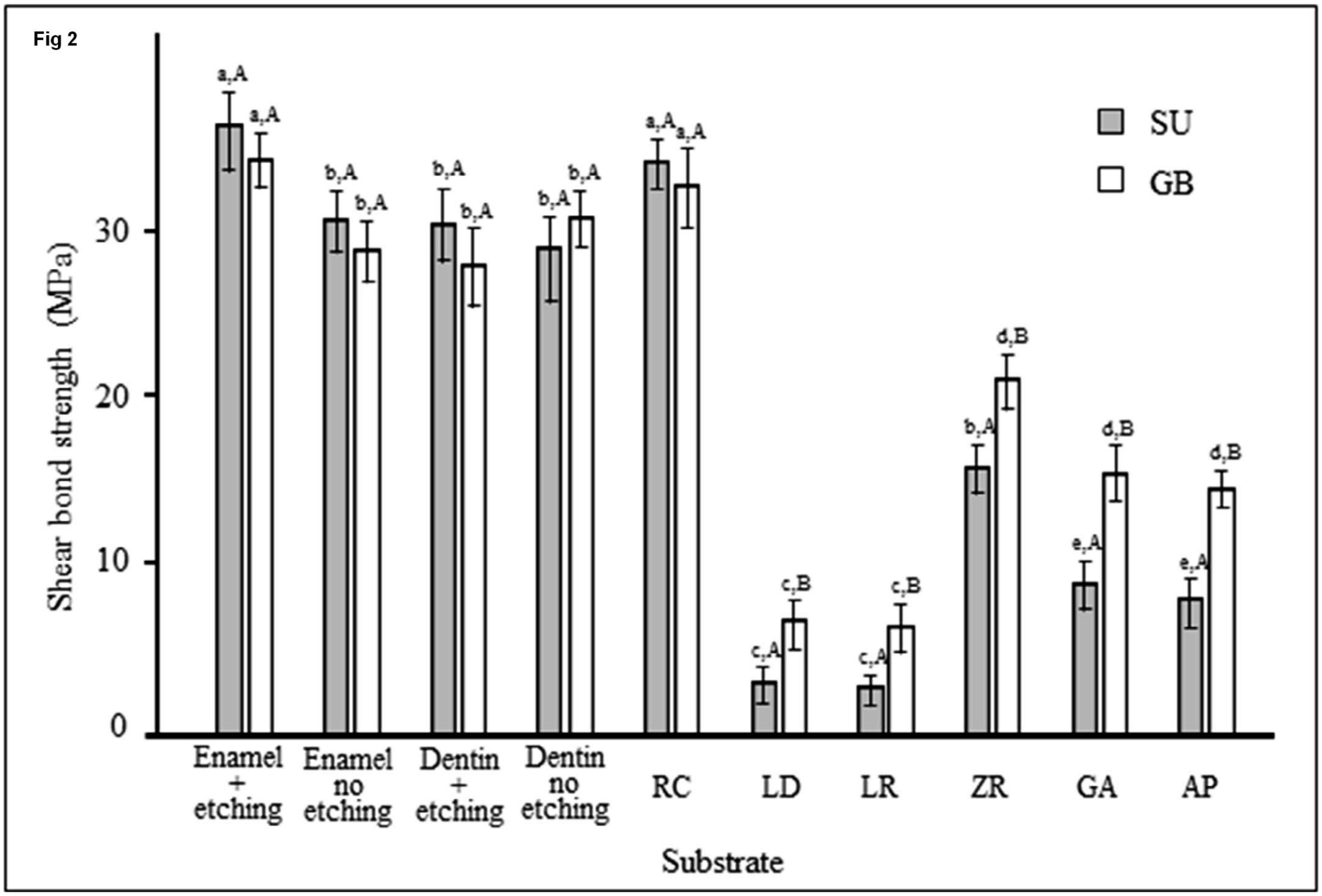

Figure 2. *Influence of type of substrate on the shear bond strength (MPa) of universal adhesives after 10,000 thermal cycles. The same lowercase letter indicates no significant differences between types of substrate. The same capital letter indicates no significant differences between adhesives. Abbreviations: SU, Scotchbond Universal; GB, G-Premio Bond; RC, resin composite; LD, lithium disilicate; LR, leucite reinforced; ZR, zirconia; GA, gold alloy, AP, gold-palladium.*

Table 4: *Failure Mode Analysis of Debonded Specimens after Shear Bond Strength Tests of Universal Adhesives with Various Substrates*[a]

Substrate	24 h group		TC group	
	SU	GB	SU	GB
Enamel (etching)	[23/2/0/0]	[23/2/0/0]	[20/3/1/1]	[20/4/1/0]
Enamel (no etching)	[23/2/0/0]	[20/4/1/0]	[23/0/1/1]	[23/0/1/1]
Dentin (etching)	[20/3/2/0]	[21/2/2/0]	[20/2/3/0]	[21/2/2/0]
Dentin (no etching)	[19/4/2/0]	[23/1/1/0]	[23/2/0/0]	[20/1/2/1]
Resin composite	[19/1/5/0]	[19/0/5/1]	[19/0/4/2]	[21/0/3/1]
Lithium disilicate	[25/0/0/0]	[25/0/0/0]	[25/0/0/0]	[25/0/0/0]
Leucite glass ceramic	[25/0/0/0]	[25/0/0/0]	[25/0/0/0]	[25/0/0/0]
Zirconia	[25/0/2/0]	[23/0/2/0]	[25/0/0/0]	[25/0/0/0]
Type III gold alloy	[25/0/0/0]	[30/0/0/0]	[25/0/0/0]	[25/0/0/0]
Au-Ag-Pd alloy	[25/0/0/0]	[25/0/0/0]	[25/0/0/0]	[25/0/0/0]

Abbreviations: Au-Ag-Pd alloy, gold, silver, palladium alloy; GB, G-Premio Bond; SU, Scotchbond Universal; TCs, thermal cycles.
[a] [ ] Indicates failure mode [adhesive failure/cohesive failure in substrate/cohesive failure in resin/mixed failure].

factors for success with universal adhesives is the chemical bonding capability of their functional monomers to various substrates.[3-7] Therefore, the chemical bonding potential between the adhesive and various substrates may have a greater influence on the bond durability of universal adhesives than do their surface modification and coating effects.

The SBSs of universal adhesives to enamel with phosphoric acid pre-etching of 24 h and TC groups were significantly higher than those without phosphoric acid pre-etching and did not depend on the type of adhesive. Over the years, phosphoric acid pre-etching has become the standard procedure for enamel conditioning to improve surface characteristics prior to the application of adhesive bonding agents.[25] Phosphoric acid pre-etching of enamel increases not only the bonding area but also the wettability of the adherent surface.[26] In addition, the surface free energy of enamel with phosphoric acid pre-etching was significantly higher than that of enamel without phosphoric acid pre-etching in the present study. The evidence from several studies,[3,27,28] including the current study, clearly shows an increase of enamel bond strength following phosphoric acid pre-etching.

The SBSs of universal adhesives to dentin with and without phosphoric acid pre-etching of each of the 24 h and TC groups were similar and did not depend on the type of adhesive. Previous studies[3,29] have demonstrated that the MDP in universal adhesive allows for stable bonding to dentin regardless of the presence or absence of phosphoric acid pre-etching. This monomer forms a stable nanolayer together with a deposition of stable MDP–calcium salts at the adhesive interface regardless of the presence or absence of phosphoric acid pre-etching, which increases the bond strength of the adhesive interface.[30] SU also contains a specific polyalkenoic acid copolymer (Vitrebond copolymer) used in the resin-modified glass ionomer Vitrebond (3M ESPE).[31] Vitrebond copolymer bonds chemically and spontaneously to hydroxyapatite, and a previous study[32] demonstrated a higher bond strength for an adhesive containing it than for an adhesive without the Vitrebond copolymer. On the other hand, GB also contains 4–methacryloxyethyl trimellitic acid (4-MET) as a functional monomer. It has been reported[33] that 4-MET has a strong chemical bonding potential to calcium-containing substrates, similar to MDP. Therefore, chemical interactions between hydroxyapatite and specific components of the adhesive can be thought to lead to the higher SBS of universal adhesives to dentin regardless of the presence or absence of phosphoric acid pre-etching.

The SBSs to enamel and dentin of TC group were higher than those of 24 h group, regardless of the presence or absence of phosphoric acid pre-etching. The mechanical properties of the adhesive interface might improve over time as a result of post-curing within the adhesive and the resin composites, resulting in SBS to enamel and dentin of TC group that is higher than that of 24 h group.

The SBS of the universal adhesives to RC of 24 h and TC groups did not show any significant differences depending on the type of adhesive used. For composite-composite bonding, a previous study[34] has suggested that the use of an intermediary layer is beneficial to improve surface wetting and chemical bonding, regardless of the texture created by the mechanical surface treatment. The use of an intermediary layer purportedly enhances composite-composite bonding by promoting chemical coupling to the resin matrix, chemical bonds to the exposed filler particles, and micromechanical retention through monomer penetration into the microstructure of the resin composite.[35] This may be why universal adhesive creates a strong bond between cured resin composite and newly applied resin composite.

The SBSs of universal adhesives to LD and LR of TC group were significantly decreased compared to those of 24 h group. The use of silane coupling agents in enhancing the bond of resin composite to silica-based ceramics is widely accepted[36] and thus is used with universal adhesives for bonding to ceramics.[6,37] Silane is a dual functional monomer consisting of a silanol group that reacts with the ceramic surface and a methacrylate group that co-polymerizes with the adhesives.[38] However, it has been reported[36] that a rapid increase in the amount of water absorbed by the adhesive interface causes hydrolysis and degradation of the silane. Water storage and thermal cycling have been described[39] as detrimental for silane-ceramic bonding. In addition, it has been reported[40] that silanized interfaces appear to be unstable in humid conditions, and the silane bond was found to deteriorate in moisture. Since the current adhesives are permeable to water, the silane-ceramic bond is expected to deteriorate by hydrolysis over time. Therefore, it appears that the SBS of universal adhesive to LD and LR of TC group is influenced by the detrimental effects on silane-ceramic bonding from the thermal cycling. SU contains silane and MDP monomer, which aids in the adhesion of resin to ceramics, and thus this adhesive is capable of bonding with ceramics without the addition of any silanating step.[6] This kind of universal adhesive provides a new, simplified approach to bonding between resins and ceramics.[37] However, the results of the present study show that GB, which requires an additional silanating step prior to applying the universal adhesive, has a higher SBS of 24 h and TC groups than does SU. Therefore, this result suggests that when applying a universal adhesive, an additional silanating step may be valuable for optimizing the ceramic-resin bond even with universal adhesives.

The present study showed that the SBS of universal adhesives to ZR of 24 h and TC groups was significantly higher than that of LD and LR, and the universal adhesives bonded well to zirconia. MDP has also been shown[41] to be effective in improving resin bonding to zirconia. It has been assumed that the hydroxyl groups of the phosphate moiety in MDP interact with the hydroxyl groups on the zirconia surface through Van der Waals forces or hydrogen bonds.[5] Therefore, the results for SBS to ZR for universal adhesives may be explained by the chemical bonding affinity between MDP and zirconia. In addition, the SBS of SU of 24 h group was significantly higher than that of GB. Silane cannot contribute to the chemical bond to zirconia because zirconia lacks silica. However, silane could increase the wettability of the zirconia surface and as a result improve the initial bond strength.[42] However, in spite of the high SBS of 24 h group, SU showed a significantly lower SBS to zirconia than did GB of TC group. The silane may increase the hydrophilicity of SU, thereby predisposing the adhesive layer to hydrolytic degradation. This hypothesis needs further investigation.

The SBSs to GA and AP of GC of 24 h and TC groups were significantly higher than those of SU. Generally, metal elements are classified into two categories: noble metals (e.g., gold, palladium, or silver) and base metals (e.g., copper and aluminum).[43] For bonding to noble metals, methacrylate monomers that contain sulfur have been synthesized and used clinically.[44] A methacryloxyalkyl thiophosphate methylmethacrylate, a sulfur-containing monomer, is used in GB to improve bonding with noble metals. In contrast to noble metals, base metals are characterized by an oxide layer, which is created on the metal surface in an atmospheric environment. Although MDP chemically bonds to oxidized base metals, the base metal content of GA and AP typically only ranges from 15% to 20%. These results suggest that universal adhesives employing sulfur-containing monomers together with a phosphate monomer may be effective for bonding with dental metals. According to the results of this study, the other null hypothesis, that there would not be differences in bond durability of universal adhesive to various substrates, can also be rejected.

The results of this study suggest that universal adhesives modify the interfacial characteristics of a wide range of substrates and create a consistent surface, but that the bond durability of universal adhesive to various substrates differs depending on the type of substrate and the adhesive. Therefore, it is crucial for general practitioners who use universal adhesives to understand the factors that contribute to the bond durability with various substrates and to be aware of the chemical bonding potential between adhesives and substrates.

CONCLUSIONS

The results of this study suggest that the interfacial characteristics of the untreated surfaces of the various substrates show significant differences depending on the type of substrate, but that the interfacial characterics of substrates treated by universal adhesive after light irradiation do not show any significant differences regardless of the substrate used. The interfacial characteristics of substrates treated by universal adhesive after light irradiation were closer to those of resin composite than those of various substrates. This modifying and coating ability of universal adhesives is expected to contribute to the bond durability of universal adhesive with various substrates, especially in an adhesive-resin composite interface. However, the bond durability of universal adhesives to various substrates differs depending on the type of substrate and the adhesive used and is particularly variable with glass ceramics, zirconia, and metal alloys. This indicates that the difference in bond durability was strongly influenced by the chemical bonding potential between substrates and universal adhesives.

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Regulatory Statement

This study was conducted in accordance with all of the provisions of the local human subjects oversight committee guidelines and policies of the Ethics Committee for Human and Animal Studies at Nihon University School of Dentistry in Tokyo, Japan. The approval code for this study is 2014-10.

Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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