Influence of photoirradiation conditions on dentin bond durability and interfacial characteristics of universal adhesives

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The influence of photoirradiation conditions on dentin bond durability and interfacial characteristics of universal adhesives was investigated. Universal adhesives were applied to the dentin surfaces and photoirradiated with 100 mW/cm² for 40 s, 200 mW/cm² for 20 s, and 400 mW/cm² for 10 s. A resin composite was bonded to dentin to determine shear bond strength after 24 h water storage and 30,000 thermal cycles, and water contact angle of cured adhesive were measured by the sessile drop method. Greater dentin bond strengths after 24 h water storage and 30,000 thermal cycles were achieved under these conditions at light intensity exceeding 200 mW/cm². The results of this study suggested that the photoirradiation conditions affect the dentin bond durability and interfacial characteristics of universal adhesives even at the same total energy.

Keywords: Universal adhesive, Dentin bond durability, Interfacial characteristics, Light intensity, Photoirradiation time

INTRODUCTION

The latest adhesive systems require fewer and simpler application steps and have shorter application times in clinical settings1, leading to time-saving options such as single-step self-etch adhesives2. Recent trend in adhesive systems is the use of the so-called universal adhesive which can be used with total-etch, self-etch, or selective-etch techniques3, and can also be used to bond to a variety of substrates4. These simplified adhesives consist of acidic functional, hydrophilic, hydrophobic monomers in addition to solvent, water, and fillers5. Water, in particular, plays essential role in ensuring the ionization of acidic functional monomers, while added organic solvents facilitate mixing between hydrophilic and hydrophobic components6. However, the incorporation of water and solvents into the adhesive may reduce its mechanical properties, decreasing bond durability7. Therefore, their removal from universal adhesives before photoirradiation is important for optimal bonds.

Current simplified adhesives present high hydrophilicity even after polymerization, which may increase their solubility and water uptake compared with their conventional multistep equivalents8. Long-term water leaching into adhesives may further compromise their mechanical properties, affecting dentin bond durability9. These phenomena may depend on the polymerization rate of the adhesive, which relies on the total energy per unit area at the adhesive surface. This energy density, which is calculated by multiplying the light intensity by the total photoirradiation time during curing10, varies according to clinical situations such as cavity preparation, tooth position, and existing adjacent teeth11. It decreases when the distance between the light tip and cavity wall increases12. According to a previous study, such a reduction in energy density causes lower dentin bond strength in single-step self-etch adhesives, and adequate bond strength requires an energy density surpassing 4,000 mJ/cm²13. In addition, the observed dentin bond strength of single-step self-etch adhesives was strongly related with the interfacial characteristics of cured adhesive, and these parameters were affected by the light intensity of the curing unit14.

Polymerization kinetics also plays an important role in the mechanical properties of adhesives15. Functional monomers generate a highly cross-linked network upon polymerization16. A higher polymerization rate typically strengthens the mechanical properties of the adhesive layer, enhancing bond durability17. Polymerization depends on light intensity and photoinduced temperature increase18, which diminish when the distance between the light tip and the materials increases19,20. Therefore, longer photoirradiation times are recommended for tooth positions where photoirradiation is hard to achieve, such as the distal aspect of the molars and lingual aspect of the mandibular incisors21. Longer photoirradiation times can compensate for reduced light intensity in terms of energy density22. However, this assumes that a certain total energy density level produces enough free radicals in the adhesive. For instance, polymerization of adhesive might depend on reaching a certain energy density level of free radicals, or a certain temperature, and changes in light intensity and photoirradiation time could affect either of these factors. Further, the effects on polymerization of an adhesive could depend on the composition of the adhesives, particularly the nature of the photo initiators or functional monomers, and on the
bonding environment. Thus, it is important to look at the influence of different photoirradiation conditions at constant total energy on the dentin bond durability of universal adhesives.

This study aims to evaluate the influence of photoirradiation conditions on dentin bond durability and interfacial characteristics of universal adhesives. The null hypothesis to be tested was that photoirradiation conditions, which achieve an energy density of 4,000 mJ/cm², should not affect the dentin bond durability and interfacial characteristics of universal adhesives.

MATERIALS AND METHODS

Adhesive systems
Three universal adhesives used were Scotchbond Universal (SU, 3M, St. Paul, MN, USA), G-Premio Bond (GB, GC, Tokyo, Japan), and All-Bond Universal (AU, BISCO, Schaumburg, IL, USA). Adhesives are listed in Table 1 along with these associated lot numbers and components are shown. Ultra-Etch (Ultradent, South Jordan, UT, USA) was used as a 35% phosphoric acid pre-etching agent.

Shear bond strength tests
The shear bond strength of three universal adhesives to dentin with and without phosphoric acid pre-etching was measured by a notched-edge test (ISO 29022)²³. Bovine mandibular incisors extracted from 2–3 year old cattle and stored frozen (–20°C) for up to 2 weeks. Roots were cut off using a slow-speed saw equipped with a diamond-impregnated disk (Isomet, Buehler, Lake Bluff, IL, USA) before the pulps were removed. Subsequently, each tooth pulp chamber was filled with cotton to avoid penetration of the embedding media. Excess debris was eliminated by ultrasonic cleaning after 30 s in distilled water and surfaces were washed and dried with oil-free compressed air. Each tooth was then mounted in self-curing acrylic resin (Tray Resin II, SHOFU, Kyoto, Japan) and placed under water to limit the temperature rise caused by the exothermic polymerization of the acrylic resin. The dentin bonding surfaces were ground flat using a grinder-polisher (Ecomet 4, Buehler) and a sequence of silicon carbide (SiC) papers (P180 and P320, as specified by ISO 29022) (Struers, Cleveland, OH, USA). These surfaces were then washed and dried with oil-free compressed air. Dentin surfaces were prepared by phosphoric acid etching for 15 s before adhesive application (with pre-etching), while surfaces without phosphoric acid pre-etching were also prepared (without pre-etching). These procedures were conducted under ambient conditions [(23±2)ºC at (50±10)% relative humidity] to produce 30 specimens with or without pre-etching using three universal adhesives.

Shear bond strengths were evaluated using an Ultradent Bonding Assembly (Ultradent). Adhesives were applied to dentin surfaces according to the manufacturers’ instructions before photoirradiation. Each adhesive was photoirradiated at standardized distance of 2 mm with a quartz-tungsten halogen unit (Optilux 501, Kerr, Orange, CA, USA) with various combinations of light intensity and photoirradiation time to achieve a constant energy density of 4,000 mJ/cm². The quartz-tungsten halogen unit was connected to a variable voltage transformer (Type S-130-10, Yamabishi Electric, Tokyo, Japan). The light intensities were set to 100, 200, 400 and 600 mW/cm² using a radiometer.

Table 1  Materials used in this study

<table>
<thead>
<tr>
<th>Materials (Lot. No)</th>
<th>Type of material (Code)</th>
<th>Main components</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotchbond Universal (566724)</td>
<td>Universal Adhesive (SU)</td>
<td>MDP, Bis-GMA, HEMA, Vitrebond copolymer, polyethylene glycol, water, initiator, colloidal silica, silane</td>
<td>3M, St. Paul, MN, USA</td>
</tr>
<tr>
<td>G-Premio Bond (541424)</td>
<td>Universal Adhesive (GB)</td>
<td>MDP, 4-MET, MEPS, Methacrylate monomer, acetone, water, initiator, silica</td>
<td>GC, Tokyo, Japan</td>
</tr>
<tr>
<td>All-Bond Universal (1312131)</td>
<td>Universal Adhesive (AU)</td>
<td>MDP, Bis-GMA, HEMA, ethanol, water, initiator, silanated colloidal silica</td>
<td>BISCO, Schaumburg, IL, USA</td>
</tr>
<tr>
<td>Ultra-Etch (G019)</td>
<td>Pre-etching agent</td>
<td>35% phosphoric acid</td>
<td>Ultradent, South Jordan, UT, USA</td>
</tr>
<tr>
<td>Clearfil AP-X (Shade: A2, 1312131)</td>
<td>Resin Composite</td>
<td>Bis-GMA, TEGDMA, silanated barium filler, silanated colloidal silica, dl-Camphorquinone, catalysts, accelerators, pigments, others</td>
<td>Kuraray Noritake Dental, Tokyo, Japan</td>
</tr>
</tbody>
</table>

MDP: 10-methacryloyloxydecyl dihydrogen phosphate, Bis-GMA: bisphenol-A-glycidyl methacrylate, HEMA: 2-hydroxyethyl methacrylate, 4-MET: 4-methacryloyloxyethyl trimellitic acid, MEPS: Methacryloyloxyalkyl thiophosphate methylmethacrylate, TEGDMA: triethyleneglycol dimethacrylate
(model 100, Kerr). Therefore, chosen photoirradiation conditions were 100 mW/cm² for 40 s (100 mW/cm²), 200 mW/cm² for 20 s (200 mW/cm²), and 400 mW/cm² for 10 s (400 mW/cm²). After application of the adhesive to the bonding sites, plastic molds (measuring 2.38 mm in internal diameter and approximately 2.5 mm in height) were clamped to the fixture against the dentin surfaces and filled with resin composite (Clearfil AP-X, Kuraray Noritake Dental, Tokyo, Japan) using a condenser. The resin composite was subsequently photoirradiated for 30 s at standardized distance of 2 mm with a quartz-tungsten halogen unit set at a light intensity of 600 mW/cm². The plastic mold was removed and the finished specimens were transferred to distilled water and stored at 37°C for 24 h. The specimens were randomly allocated to two groups (n=15 per group): (1) no thermal cycling (24 h group); (2) 30,000 thermal cycles between 5 and 60°C (TC group). Thermal cycling was conducted using a thermal shock tester (TTS-1 LM, Thomas Kagaku, Tokyo, Japan). Each cycle consisted of water bath incubation lasting 30 s, with a transfer time of 5 s.

Measurement were performed using a universal testing machine (5500R, Instron Worldwide Headquarters, Norwood, MA, USA) equipped with an Ultradrant shearing fixture at a crosshead speed of 1.0 mm/min. The shear bond strengths (MPa) were calculated by dividing the peak load at failure by the bonding area. After testing, the specimens were examined by optical microscopy (SZH-131, Olympus, Tokyo, Japan) at a magnification of x10 to determine the type of the bond failure. The proportions of the resin composite surface with adherent dentin and visible residues were estimated to classify the failure as adhesive failure; cohesive failure in dentin, cohesive failure in resin composite and mixed failure (combination of adhesive and cohesive failure).

**Water contact angle measurement**
Mandibular incisors from cattle were prepared as described above (Shear bond strength tests) and adhesives were applied to the dentin surfaces with and without pre-etching according to the manufacturers’ instruction before photoirradiation (n=10). Each adhesive was photoirradiated at a standardized distance of 2 mm and at 100, 200 and 400 mW/cm² to achieve a constant amount of light energy of 4,000 mJ/cm². The equilibrium water contact angle was measured by the sessile drop method under ambient conditions [(23±2)°C at (50±10)% relative humidity] using a contact angle measurement apparatus (DM 500, Kyowa Interface Science, Saitama, Japan) for 10 specimens per photoirradiation condition. The apparatus was fitted with a charge-coupled device camera to enable automatic measurement. A standardized 3.0 µL drop of distilled water was placed on the cured adhesive surface and a profile image was captured after 500 ms using the apparatus. Water contact angles were then calculated by 0/2 method using the built-in interface measurement and analysis system (FAMAS, Kyowa Interface Science).

**Statistical analysis**
The shear bond strength and water contact angle data were analyzed using a three-way analysis of variance (ANOVA) followed by Tukey’s post hoc test (α=0.05). The ANOVA and Tukey’s test were completed using a commercial statistical software package (SPSS Statistics Base, International Business Machines, Armonk, NY, USA). Results were analyzed using a commercial statistical software package (SPSS Statistics Base). A complex chi-square test was used to statistically analyze the failure mode; it was conducted using the SPSS Statistics Base software package.

**RESULTS**
Shear bond strengths of universal adhesives to dentin with and without pre-etching photoirradiated under different conditions of 24 h and TC groups are shown in Figs. 1 and 2, respectively. The three-way ANOVA revealed that photoirradiation conditions displayed a
significant influence \((p<0.05)\) on shear bond strengths, unlike the adhesive type and pre-etching \((p>0.05)\). The interaction between photoirradiation conditions and adhesive type was also more significant than that among others. Regardless of pre-etching, universal adhesives presented higher shear bond strengths of 24 h group at light intensities exceeding 200 mW/cm² (25.1–30.1 MPa) than at 100 mW/cm² (17.9–20.1 MPa) for the same energy density (Fig. 1). Similarly, shear bond strengths of TC group at light intensities surpassing 200 mW/cm² (21.5–25.2 MPa) exceeded those at 100 mW/cm² (9.2–13.2 MPa) for same energy density (Fig. 2). Failure mode analysis of debonded specimens of 24 h and TC groups are shown in Table 2. The failure type was not associated with shear bond strength and adhesive failure was predominant. A chi-squared test revealed no significant differences in failure mode among photoirradiation conditions, adhesive type, and presence or absence of pre-etching.
Table 3  WCA values of universal adhesives with and without phosphoric acid pre-etching under different photoirradiation conditions

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Pre-etching</th>
<th>Photoirradiation condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>100 mW/cm²×40 s</td>
</tr>
<tr>
<td>SU</td>
<td>with</td>
<td>40.5 (2.2)a,A</td>
</tr>
<tr>
<td></td>
<td>without</td>
<td>39.7 (2.4)a,A</td>
</tr>
<tr>
<td>GB</td>
<td>with</td>
<td>37.5 (2.1)a,A</td>
</tr>
<tr>
<td></td>
<td>without</td>
<td>36.5 (2.7)a,A</td>
</tr>
<tr>
<td>AU</td>
<td>with</td>
<td>42.1 (2.1)c,A</td>
</tr>
<tr>
<td></td>
<td>without</td>
<td>42.9 (3.0)c,A</td>
</tr>
</tbody>
</table>

Unit: °, values in parenthesis are standard deviations. Same small letter in same vertical column indicates no significant difference (p>0.05). Same capital letter within individual rows indicates no significant difference (p>0.05).

Fig. 3  Representative scanning electron microscopy images of debonded specimens after shear bond strength tests at 1,000× magnification. The debonded specimens showed predominantly adhesive failure and debonding at the interface between dentin and the adhesive can be clearly observed regardless of the photoirradiation conditions and pre-etching. Fracture surfaces of the specimens photoirradiated at 100 mW/cm², large numbers of voids were observed when compared to specimens photoirradiated at 200 and 400 mW/cm² regardless of phosphoric acid pre-etching.
Fig. 4 Representative field-emission scanning electron microscopy images of the resin-dentin interface at 5,000× magnification. The resin-dentin interface of each photoirradiation condition showed excellent adaptation regardless of the presence or absence of phosphoric acid pre-etching. Specimens irradiated at a weaker light intensity of 100 mW/cm² had a lesser adhesive thickness. R: resin composite; A: adhesive layer; HL: hybrid layer; D: dentin.

DISCUSSION

According to a previous study, the dentin bond strength...
of single-step self-etch adhesives increases with increasing energy density at a fixed light irradiation time of 10 s, and an energy density exceeding 4,000 mJ/cm² at the adhesive is necessary to achieve adequate bond strength¹². The bonding performance of adhesives have been compared for different energy densities²⁴,¹¹,¹²,²⁵. Here, the dentin bond durability of universal adhesives were investigated at a constant energy density of 4,000 mJ/cm² by changing light intensities and photoirradiation times.

Regardless of pre-etching, shear bond strengths of universal adhesives to dentin of 24 h and TC groups at 200 mW/cm² or above were higher than those at 100 mW/cm², even with the same energy density. A previous study reported that the hydrophobicity of adhesive is essential in durable bonds, and incomplete polymerization leads to interface degradation and decreased dentin bond durability²⁰. Incomplete polymerization of adhesive can accelerate the water degradation effects, leading to bond deterioration²⁷. From the results of water contact angle of cured adhesive with different photoirradiation conditions, universal adhesives photoirradiated at light intensities of 100 mW/cm² presented significantly lower water contact angle than those photoirradiated at 200 mW/cm² or above, demonstrating their greater hydrophilicity. This indicates the incomplete polymerization of the adhesive at 100 mW/cm² due to the higher hydrophilicity even at a constant energy density of 4,000 mJ/cm². Previous studies reported that differences in photoirradiation conditions affect the kinetics of polymerization¹⁶,²⁹. Monomers in adhesives form into a highly cross-linked network upon polymerization, reducing the hydrophilicity of the adhesive¹⁵,¹³. The complete polymerization of monomers present in universal adhesives is expected to lower the hydrophilicity of the adhesive. Therefore incomplete polymerization of the adhesives at 100 mW/cm² may be one of the reasons why the weaker dentin bond durability at 100 mW/cm² were observed compared to those at 200 mW/cm² or above regardless of the adhesive type and pre-etching. In the SEM observations of fracture surfaces of debonded specimens at 100 mW/cm² of TC group, large numbers of voids were observed, unlike in observations of the specimens at 200 mW/cm² or above regardless of pre-etching. A previous study which investigates the relationship between degree of conversion of adhesive and bond strength reported that a low degree of conversion of adhesives increase permeability and induce phase separation of adhesive layer²⁹. Consequently, the observed large numbers of voids might be related to incomplete polymerization of the adhesives and have weak points of the specimens at 100 mW/cm², and adversely affected their bond durability. In addition, SEM observations of the resin-dentin interface show that the adhesive layer was considerably thinner under photoirradiation at 100 mW/cm² regardless of pre-etching. This suggests that low-intensity photoirradiation (below 100 mW/cm²) limits the polymerization process, creating thicker uncured adhesive potion. Therefore, this largely liquid layer may be displaced upon resin composite application, leading to the thin adhesive layer observed. A previous study reported that the thickness of universal adhesives is around 10 µm thick, and insufficient thickness of the adhesive layer have been seen as contributing to lower bonding performance³⁰. Therefore the observed insufficient thickness of adhesive layer at 100 mW/cm² might impair the bond durability of universal adhesive. The results of bond strength test, and SEM observation of fracture surfaces and adhesives interfaces suggest that the difference of photoirradiation conditions at constant total energy influences the bond durability of universal adhesive.

Although the results of shear bond strength of universal adhesives to dentin of 24 h and TC group show different tendencies among the different photoirradiation conditions, there were no significant differences in failure type depending on the photoirradiation conditions, storage conditions, type of adhesive and pre-etching, and adhesive failures were observed most frequently. A previous study has stated that an increased incidence of adhesive failure in bond strength tests was desirable to provide more relevant information about the mean bond strength³¹. Therefore, in this study, the type of failure observed may provide evidence for the clinical relevance of the measured shear bond strengths of universal adhesives using different photoirradiation conditions.

According to the results of this study, the null hypothesis, that photoirradiation conditions, which achieve an energy density of 4,000 mJ/cm², should not affect the dentin bond durability and interfacial characteristics of universal adhesives, was rejected. Overall, augmenting light intensity while maintaining the same energy density, the water contact angle and thickness of universal adhesives was increased due to the enhanced polymerization of these adhesives. Sufficient light intensity may enhance the polymerization reaction of the universal adhesive, leading to greater dentin durability of the adhesive. On the other hand, universal adhesives photoirradiated at 100 mW/cm² exhibited higher hydrophilicity, leading to inferior bond durability. Therefore, the bond durability and interfacial characteristics of universal adhesives strongly rely on the light intensity and irradiation time even at a constant energy density.

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