Recently, improvement of the properties of dentin surface using dental lasers to increase bonding strength has been anticipated in the field of adhesive dentistry. The objective of this study was to investigate changes in the surface properties of human dentin after ArF excimer laser irradiation at different irradiation times, pulse repetition rates and energy densities. The SEM images of the irradiated surfaces were observed, and the contact angle and the roughness of the irradiated surface were measured. As a result, SEM demonstrated that the dentin surface became irregular following ArF excimer laser irradiation. When the energy density increased, the irregularity became more minute and dentinal tubules were more easily identified. By contrast, such changes were not observed when the irradiation time and pulse repetition rate were changed. Moreover, as energy densities increased, the contact angle tended to decrease and the surface roughness tended to increase. These results suggested that the area of the irradiated surface and wettability increased after irradiation with the ArF excimer laser. Consequently, irradiation with ArF excimer lasers could improve the surface properties and be potentially useful for adhesive dentistry.

Key words: ArF excimer laser, human dentin, SEM image, contact angle, surface roughness

Introduction

At present, various lasers are used in dental clinics. For example, while there have been reports of the use of Er:YAG and CO\textsubscript{2} lasers as devices for hard tissue treatment, thermal damage in the irradiation area from Er:YAG and CO\textsubscript{2} lasers has also been demonstrated\textsuperscript{5-12}. On the other hand, there are several other kinds of lasers that have not been used in dentistry despite their potential usefulness as a dental device. For example, ArF excimer lasers are frequently used in ophthalmology or industry\textsuperscript{13-15}. The ArF excimer laser utilizes the ultraviolet wavelength. The short-wavelength laser is believed to provide sufficient energy to directly cut covalent molecular bonds with less thermal damage compared with Er:YAG or CO\textsubscript{2} lasers\textsuperscript{15,16}.

Our research group has examined the dentin surface after ArF excimer laser irradiation using scanning electron microscopy (SEM) and element analysis (energy dispersive X-ray spectroscopy: EDS). As a result, it was revealed that this laser could excavate dentin at low energy, and that the irradiated area was less carbonized compared with that of Er:YAG or CO\textsubscript{2} lasers\textsuperscript{17}. Furthermore, in the processing of organic material, the ArF excimer laser was used to improve surface properties, such as wettability, before adhesion\textsuperscript{18,20}. The dentin matrix was an organic material. Therefore, it could be hypothesized that the surface properties would be improved by irradiation with the ArF...
excimer laser, which could contribute to adhesive dentistry. In the present study, the dentin surfaces were observed using SEM, and the contact angle and the surface roughness of the dentin surface were measured after irradiation with the ArF excimer laser under several different conditions, to elucidate the effect of ArF excimer laser irradiation towards the improvement of dentin surface properties.

**Materials and Methods**

**Specimen preparation**

Human wisdom teeth without caries were used for specimen preparation. Sixteen teeth were extracted for pericoronitis after obtaining the donors’ consent for experimental use. Each tooth was washed by current water, sealed in polyethylene packages and stored in a freezer at –15 °C. Each tooth was defrosted at room temperature (23 °C) prior to use. All of the teeth were used within one month after the extraction.

Each tooth was cut in parallel with the tooth axis and in the mesiodistal direction with a low-speed cutting machine (ISOMET1000®, Buehler, USA) to generate two flat dentin surfaces. The surfaces were polished with #1200 wet abrasive paper. Three dentin surfaces from three different teeth were used for the SEM observation. Twenty-five dentin surfaces were classified into five groups and were used for the contact angle and the roughness tests; each group consisted of five dentin surfaces from different teeth. In a dentin surface, the coronal dentin between occlusal enamel and pulp cavity was used as the area of the laser irradiation in the following procedure.

**Laser Irradiation**

An ArF excimer laser generator, EX5 Excimer Laser® (GAM Laser, USA) was used. The beam size of this laser was 6 × 3 mm, the wavelength was 193 nm, and the pulse length was 10 ns. The irradiating conditions are shown in Table 1. The irradiation time and the pulse repetition rate were altered using a controller on the generator. A scheme of the laser irradiation is presented in Fig. 1. The voltage for emission was fixed at 15.0 kV at the generator. The energy density was controlled by changing the irradiated area by moving the collective lens, located between the generator and target; the energy densities for each pulse were calculated from the area and amount of energy at the target in preliminary experiments.

For SEM observation, the laser irradiation fields of three dentin surfaces were irradiated under conditions 1 to 9. Different locations on the surfaces were exposed to the laser irradiation for each condition. A non-irradiated area of one of the dentin surfaces was observed as the control.

For the contact angle test and surface roughness test, the laser was irradiated on the irradiation fields of the dentin surfaces of four groups under conditions 1, 7, 8, and 9, respectively. The remaining single group was used as control.

**SEM observation**

Each irradiated surface was coated with Palladium using an ion coater (Ion Coater IB-5®, Eiko, Japan) and observed using SEM (S-4500®, Hitachi, Japan).

**Contact angle test**

A 1 μl aliquot of pure water was dropped on the irradiated surfaces and the contact angles were measured immediately after dropping and five seconds after dropping using a surface analysis system VCA Optima – XE® (AST, USA). For conditions 1, 7, 8, 9 and control, three different locations were randomly

<table>
<thead>
<tr>
<th>Condition No.</th>
<th>irradiation time (sec)</th>
<th>pulse repetition rate (pps)</th>
<th>energy density (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>20</td>
<td>47.6</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>40</td>
<td>47.6</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>60</td>
<td>47.6</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>20</td>
<td>47.6</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>40</td>
<td>47.6</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>60</td>
<td>47.6</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>20</td>
<td>71.4</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>20</td>
<td>144.9</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>20</td>
<td>217.4</td>
</tr>
</tbody>
</table>
selected for one surface for the measurement and were averaged, respectively. The average of the five averaged values obtained from five surfaces was regarded as the contact angle for each condition.

Surface roughness test
For one irradiated surface, surface roughness (Ra) was measured for three randomly selected locations 400 μm in length using an optical 3D measurement device IF–0201® (aicona imaging, Germany) and averaged for conditions 1, 7, 8, and control, respectively. The average of the five values obtained from five surfaces was regarded as the Ra for each condition. In the case of condition 9, the irradiated area became small and wedge-shaped. Therefore, Ra was measured at only one location in the deepest part. The average of five values obtained from five surfaces was regarded as the Ra of condition 9.

Statistical analysis
The differences of variance of the contact angle and Ra among each condition were analyzed using Levene’s test. When the variance difference was significant, the differences of the contact angle and the Ra among each condition were analyzed using Welch’s ANOVA and Tamhane’s test. When the variance difference was not significant, the differences of the contact angle and the Ra among the conditions were analyzed using one-way ANOVA and Tukey’s test. The difference of the contact angle between those immediately after dropping and five seconds after dropping were analyzed with paired t-test. Statistical analyses were performed using SPSS 14.0 J for Windows (SPSS, USA).

Results

SEM observation
All of the irradiated areas on the dentin surfaces appeared irregular without smear layer compared with the controls. When the energy density was changed, morphological differences were observed (Fig. 2B-E, Fig. 3B-E). In the 3000× magnification images, irregularity of the irradiated surface increased gradually, the boundaries of intertubular and peritubular dentin appeared more clearly, and dentinal tubules were easily identified as the energy densities increased (Fig. 2B-E). In the 30000× magnification images, the irregular features of the irradiated surface became more minute; the size of the convex structure on the surface become smaller (Fig. 3B-E).

In contrast, no remarkable changes were observed when the irradiation time and the pulse repetition rate were changed (Fig. 4).

Contact angle test
The contact angles of conditions 1, 7, 8, and control, immediately after dropping of the water were greater than those measured five seconds after dropping the water (p < 0.05, Table 2). For the contact angle measured immediately after dropping, the variance differences for each condition were not significant by Levene’s test; therefore, the contact angles were analyzed using one-way ANOVA and Tukey’s test. For the contact angle measured five seconds after dropping, the variance differences for each condition were significant by Levene’s test; therefore, the contact angles were analyzed using Welch’s ANOVA and Tamhane’s test. The contact angles decreased for conditions 7 and 8 immediately after dropping and five seconds after dropping (p < 0.05, Table 2). The contact angle of condition 9 could not be measured because of the acute angle of the surface produced by the irradiation.

Surface roughness test
The Ra increased with the energy density up to 144.9 mJ/cm² and decreased when the energy density was 217.4 mJ/cm² (Table 3). The variance differences of the Ra for each condition were significant by Levene’s test; therefore, the Ra was analyzed using Welch’s ANOVA and Tamhane’s test. Significant differences were observed for the Ra among each of the conditions, except between conditions 1 and 9, 7 and 8, 7 and 9 (p < 0.05).
Fig. 2. SEM images of the irradiated surfaces when the energy density was changed. A: control, B: condition 1, C: condition 7, D: condition 8, E: condition 9 (3000×). When the energy densities were increased, the boundaries of intertubular and peritubular dentin appeared more clearly and the dentinal tubules were easily identified. Scale bar = 10 μm.

Fig. 3. SEM images of the irradiated surfaces when the energy density was changed. A: control, B: condition 1, C: condition 7, D: condition 8, E: condition 9 (30000×). When the energy densities were increased, the irregular features of the irradiated surface became more prominent and minute. Scale bar = 1 μm.
**Fig. 4.** SEM images of the irradiated surfaces when the irradiation time and pulse repetition rate were changed. A: condition 1, B: condition 2, C: condition 3, D: condition 4, E: condition 5, F: condition 6 (30000×). The irregular features of the irradiated surface of condition 1 to 6 were not as varied as those observed when the energy density changed. Scale bar = 1 μm.

### Table 2. Result of the contact angle

<table>
<thead>
<tr>
<th>Condition No.</th>
<th>Control</th>
<th>1</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>immediately</td>
<td>63.1ab</td>
<td>45.9c</td>
<td>24.1a</td>
<td>17.9bc</td>
<td>—</td>
</tr>
<tr>
<td>SD (degree)</td>
<td>8.8</td>
<td>21.0</td>
<td>16.1</td>
<td>22.2</td>
<td>—</td>
</tr>
<tr>
<td>n</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Contact angle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>five seconds</td>
<td>52.5da</td>
<td>28.8</td>
<td>2.1d</td>
<td>0.0e</td>
<td>—</td>
</tr>
<tr>
<td>SD (degree)</td>
<td>10.6</td>
<td>21.5</td>
<td>2.9</td>
<td>0.0</td>
<td>—</td>
</tr>
<tr>
<td>n</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Means with the same superscript letters are significantly different. (p < 0.05)

### Table 3. Result of the surface roughness

<table>
<thead>
<tr>
<th>Condition No.</th>
<th>Control</th>
<th>1</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (μm)</td>
<td>37.2ghi</td>
<td>60.3hi</td>
<td>225.2hi</td>
<td>386.2hi</td>
<td>85.5hi</td>
</tr>
<tr>
<td>SD (μm)</td>
<td>2.5</td>
<td>9.3</td>
<td>65.1</td>
<td>83.3</td>
<td>17.3</td>
</tr>
<tr>
<td>n</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Means with the same superscript letters are significantly different. (p < 0.05)
Discussion

In the present study, human dentin was irradiated with an ArF excimer laser by modifying the irradiation time, the pulse repetition rate and energy density. We also observed SEM images of the irradiated area and measured the contact angle and surface roughness. By SEM image observation, the irradiated area showed irregular surfaces compared with control, under all irradiation conditions. The morphology of the irradiated area was dependent to a greater degree on the energy density, rather than irradiation time or pulse repetition rate. In industrial uses, such as processing of polymeric material, it is known that the energy densities of the ArF excimer laser must exceed a certain threshold to cause ablation in the irradiated area\textsuperscript{21}. In the present study, the energy density over time was not able to exceed the threshold for ablation when irradiation time and pulse repetition rate were increased; therefore, no remarkable changes in surface morphology were observed under conditions 1 to 6. Thus, among the parameters tested using the ArF excimer laser, energy density exhibited the greatest influence on the process of the dentin surface; therefore, the contact angle and roughness were measured only for conditions 7, 8, and 9 and control. The morphology changed remarkably when the dentin surface was irradiated using the laser under conditions 8 and 9. Consequently, the energy density threshold for efficient ArF excimer laser ablation of dentin was suggested to be between 71.4 and 144.9 mJ/cm\textsuperscript{2}.

The contact angles decreased when the energy densities were 71.4 and 144.9 mJ/cm\textsuperscript{2}; therefore, wettability of the dentin surface was improved by irradiation with the ArF excimer laser. It is generally believed that there is a close correlation between wettability and adhesion strength; adhesion strength increases as wettability improves\textsuperscript{22}. Decrease of the contact angle and increased adhesion strength have also been reported following excimer laser irradiation of polymeric material\textsuperscript{19-20}. Consequently, decreasing the contact angle of the dentin surface by irradiation using the ArF excimer laser is expected to contribute to increased adhesion strength. The contact angle decreased for five seconds after dropping water in each of the measured conditions. Therefore, it was suggested that it would take time to stabilize the contact angle of the dentin surface.

In surface roughness testing, the Ra increased with energy density except for condition 9. The Ra is determined as the sum of the absolute values of all of the areas in the chart above and below the mean line divided by the sampling length\textsuperscript{23}. In this experiment, the irregularity after irradiation may derive from the relative difference in the ablation rate of microstructures in dentin tissue. In general, it is known that peritubular dentin is highly calcified and the amount of hydroxyapatite is greater in peritubular dentin compared with intertubular dentin\textsuperscript{24,25}. Even in intertubular dentin, the degree of calcification varies\textsuperscript{24,25}. Hydroxyapatite consists of denser covalent bonds compared with the dentin matrix collagen, which includes weaker bonds, such as hydrogen bonds and intermolecular forces; therefore, the greater the hydroxyapatite content, the greater energy expenditure is required for decomposition. As a result, the efficacy of ablation changed with degree of calcification, which resulted in an increase in roughness along with the energy density. On the other hand, such selective ablation would potentially occur when the energy density changes within a certain range. Excess energy would totally decompose dentin tissue resulting in less depth variation, which might be the reason for the smaller Ra under condition 9.

The increase of irregularity, observed by SEM, and roughness following laser irradiation would result in an increase of the area of the bonding surface, which would contribute to improvement of the bonding strength of restorative material. However, when the contact angle of the adhesion surface is large, and wettability of the liquid is small, a discontinuous bonding interface called air pockets would occur and deteriorate the bonding strength\textsuperscript{22}. As mentioned above, a decrease of the contact angle by the ArF excimer laser irradiation was demonstrated in this study; i.e., wettability was improved by irradiation. Therefore, increased roughness or small irregularities would be advantageous for bonding.

Er:YAG or CO\textsubscript{2} lasers are currently used for hard tooth tissue excavation in dental treatment. The wettability of the dentin surface is also known to increase after Er:YAG or CO\textsubscript{2} laser irradiation\textsuperscript{26}. However these lasers cause increases of temperature in the irradiated area. Indeed, it has been shown that the temperature of the dentin surface of the irradiated area rises to about 200 °C by Er:YAG laser, and rises to about 700 °C by CO\textsubscript{2} laser\textsuperscript{2}. Such heat generated by laser irradiation causes thermal damage, such as carbonization, to the irradiated area. Furthermore, it has also been reported that irradiation of Er:YAG laser forms stratiform squamate structures on the surface of the dentin\textsuperscript{2-4}. The carbonization or the stratiform squamate structures induced by heat have been shown to decrease bonding strength between
dentin and restoration materials because of the dentin denaturation layer.\(^2\,\text{12}\)

Such heat denaturation of the irradiated area using the Er:YAG or CO\(_2\) lasers was intrinsically attributed to photothermal ablation in which the light energy changes into heat at the target material. Hence, the energy activating mechanism itself is a problem for traditional laser devices that must be considered to avoid heat denaturation. In contrast, the ArF excimer laser depends on photochemical ablation in which the light energy directly cuts the covalent bond without changing the light energy into heat.\(^3\) As a result, there is little thermal damage. Therefore, the ArF excimer laser has great potential for conservative hard tissue treatment. Consequently, irradiation with the ArF excimer laser would improve the surface properties, such as the wettability and the roughness, and could possibly be useful for adhesive dentistry.

**References**