Abstract: This experiment assessed the effect of elapsed time between air abrasion and bonding on tensile bond strength (TBS) between computer-aided design/computer-aided manufacturing (CAD/CAM) composite resin blocks and luting agents. Specimens were divided into eight groups classified by block type (Estelite Block or HC Block), elapsed time after air abrasion (none [D0] or 1 week [D7]), luting agent type (Estecem [ESC] or Rely X Ultimate [RLU]), and polymerization condition (chemical cured [CC] or light cured [LC]). In the CC+ESC group, TBS was significantly higher at D0 than at D7. There was also a significant difference between blocks in all groups except the LC+ESC group. Scanning electron microscopy and atomic force microscopy were used to observe the surfaces of blocks after air abrasion and indicated that blocks absorbed water in air with elapsed time, which affected TBS between CAD/CAM composite resin blocks and luting agents.

Keywords: CAD/CAM composite resin block; air abrasion; tensile bond strength; elapsed time; bonding.

Introduction
Computer-aided design/computer-aided manufacturing (CAD/CAM) technology has seen remarkable development since it was introduced to dentistry in the 1980s. These developments have improved the quality of dental restorations and now allow them to be manufactured with materials such as lithium disilicate glass ceramics, feldspar glass ceramics, leucite glass ceramics, titanium, zirconia, zirconia-reinforced lithium silicate, and composite resin (1,2). CAD/CAM composite resin crown restoration systems for premolars were included in the Japanese health insurance system in 2014, after which their use spread rapidly (1,3). However, because of rapid polymerization resulting from the high temperature and pressure of production (4,5), it is not easy to bond these restorations with luting agents, which means there is no unpolymerized layer on the surface. Some Japanese case reports noted desorption (especially early desorption) of CAD/CAM crowns. Therefore, identifying the cause of early desorption and a suitable surface pretreatment to minimize it are necessary to enable good bonding (4,6,7).

Air abrasion is one recommended pretreatment for improving adhesion between CAD/CAM composite resin blocks and luting agents. Air abrasion works by cleaning the adhesive surface, improving mechanical retention, and increasing the surface area to be bonded (8). However, although air abrasion was reported to improve the bond strength of CAD/CAM composite blocks (5,9), Yoshihara et al. (7) found that it caused cracks and desorption of filler on the surface of a CAD/CAM composite resin block, which reduced bond strength.
Arao et al. (10) reported that the type of particles and pressure used for air abrasion influenced the degree of surface damage, which affected bonding force. Hence, the optimal air abrasion method remains to be identified.

In clinical practice, the bonding operation is sometimes performed at some interval after air abrasion at the laboratory. However, past studies (5,7-10) mainly evaluated adhesion strength when bonding was performed immediately after air abrasion—the effect on bond strength of time elapsed from air abrasion to adhesion operation has not been reported. The bonding strength of a composite resin is affected (11) by water absorption in the matrix phase or filler-matrix interface (12-14). This could be exacerbated by air abrasion-induced cracks between the matrix and filler in CAD/CAM composite resin blocks (7), as water molecule accumulation was greatest at the filler-matrix interface (15). Hence, air abrasion might increase the likelihood that blocks will absorb water if they are left for a certain period. Furthermore, this water absorption occurs regardless of whether blocks are stored in water or air (16). Therefore, elapsed time after air abrasion was hypothesized to be a cause of desorption of CAD/CAM composite resin crowns, one of their major disadvantages. Determining the relationship between block change and bond strength with elapsed time is thus of considerable clinical importance.

This study investigated the effect of time elapsed from air abrasion to adhesion operation on initial tensile bond strength (TBS) between CAD/CAM composite resin blocks and luting agents. The null hypothesis was that the initial TBS of composite resin CAD/CAM block and luting agent would not be affected by the time elapsed from air abrasion to bonding.

### Materials and Methods

#### Specimen Preparation

Two types of CAD/CAM composite resin blocks (Estelite Block [ES], Tokuyama Dental, Tokyo, Japan, n = 80, and Block HC [HC], Shofu Inc., Kyoto, Japan, n = 80) (Table 1) with dimensions of 12 × 14 × 3 mm were...
used in this study. All specimens were wet polished with #1500 grit silicon-carbide paper (Nihon Kenshi Co. LTD, Hiroshima, Japan). Blocks were air abraded with 70-µm Al₂O₃ particles (Hi-alumina, Shofu) at a pressure of 0.1 MPa for 10 s at a distance of 10 mm. After air abrassion, the specimens were ultrasonically cleaned twice for 5 min in distilled water and air dried for 10 s.

**Experiment 1**

To investigate the effects of i) elapsed time after air abrasion, ii) the luting agent used, and iii) polymerization conditions on the TBS of CAD/CAM composite resin blocks, the block were randomly divided into eight groups (n = 10 each) (Fig. 1) classified by i) elapsed time after air abrasion: D0—no elapsed time after air abrasion, D7—stored for 1 week in a petri dish at 25°C and 60% humidity; ii) type of luting agent: ESC—Estecem (Tokuyama Dental), RLU—Rely X Ultimate (3M ESPE, Dental Products, St. Paul, MN, USA); and iii) polymerization conditions: LC—light cured for 20 s from the rear with a halogen irradiator (Optilux 501, SDS Kerr, Danbury, CA, USA), CC—chemical cured.

The bonded specimens were left for 5 min in darkness. To define the bonding area, pieces of 86-µm-thick adhesive tape (Nichiban Nice Tack Double-Sided Tape NW 15 × 20, Tokyo, Japan) with a circular hole (diameter, 3 mm) were placed on the surfaces of the CAD/CAM composite blocks. The exposed surfaces were then treated with the primers, in accordance with the manufacturers’ instructions (Table 1).

Stainless-steel rods (SUS 304 φ 6 × 20 mm) were air abraded with 70-µm Al₂O₃ particles at a pressure of 0.4 MPa for 20 s at a distance of 10 mm. After air abrasion, the stainless-steel rods were ultrasonically cleaned for 5 min in distilled water twice and air dried for 10 s. The luting agents were applied to the stainless-steel rods and bonded to the block by light curing or chemical curing in accordance with the polymerization conditions in iii).

After storage in a 100% humidity incubator at 37°C for 1 h, the specimens were stored in distilled water at 37°C for 24 h in darkness. To prevent deflection of the blocks during the tensile test, stainless-steel plates (14 × 15 × 2 mm) were affixed to the rear of the specimens with adhesive (Aron Alpha Toagosei, Tokyo, Japan). TBS was measured with a universal testing machine (Autograph AGS-H, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min.

**Scanning Electron Microscopy and Atomic Force Microscopy**

Field-emission scanning electron microscopy (FE-SEM: S-4500, Hitachi, Tokyo, Japan) was used to observe polished and air-abraded surfaces of each block at D0 and D7. D0 and D7 blocks were fixed on specimen tables with carbon tape and dried in a desiccator, after which they were coated with platinum and observed at both 10,000× and 1,000× magnification.

Blocks were observed by using atomic force microscopy (AFM: Nano Search microscope LEXT, Olympus, Tokyo, Japan). The surfaces of the blocks were scanned
while maintaining a constant resonance frequency (208.4-346.1 kHz) with a probe attached to the tip of the cantilever. An area of 1 × 1 μm was observed immediately after air abrasion (D0) in dynamic mode at a frequency of 0.5 Hz. The specimen was observed again under the same conditions after being stored in the AFM for 1 week, without moving the probe from the fixed point (D7).

**Experiment 2**

To investigate the effect of water absorption of CAD/CAM composite resin blocks on TBS, D7 blocks (ES: n = 10 HC: n = 10) were vacuum dried at 80°C for 18 h (D7 + Vac) with a vacuum oven (ADP 300, Yamato Scientific, Tokyo, Japan). Although the effect of water absorption was investigated in all groups, the CC + ESC group was the only group in which a significant difference was observed between D0 and D7 conditions in Experiment 1. This group was thus selected for vacuum drying, to determine whether the difference was caused by water absorption. The specimens were bonded with ESC and chemically cured. After curing, tensile tests were conducted with the method described above (Fig. 2).

**Statistical Analysis**

Statistical analyses were performed with the software package SPSS Version 22 for Windows (SPSS Inc., Chicago, IL, USA). Assessment of normality and homoscedasticity with the Shapiro-Wilk and Levene tests confirmed normality in all groups; however, not all groups showed homoscedasticity. Thus, because the number of samples were equal, parametric procedures were used. There were four factors in this experiment. Therefore, to reduce the factors one by one, t-tests were initially performed on the polymerization conditions in Experiment 1, because of past reports that bond strength values were significantly higher after light curing than after chemical curing (17,18). The data were classified in relation to polymerization conditions and analyzed with three-way analysis of variance (ANOVA) (luting agent, CAD/CAM composite resin block, and elapsed time after air abrasion). Because significant interactions between all three factors were present, the data were further analyzed by two-way ANOVA using the variables of CAD/CAM composite resin block (ES or HC) and elapsed time after air abrasion (D0 or D7). t-Tests with Bonferroni correction, which can be used regardless of the presence or absence of homoscedasticity, were used to compare values between groups.

Data from Experiment 2 and from the CC + ESC group in Experiment 1 were analyzed by two-way ANOVA using the variables of CAD/CAM composite resin block (ES or HC) and elapsed time after air abrasion (D0, D7, or D7 + Vac). t-Tests with Bonferroni correction were performed to compare values between groups. All statistical analyses were performed at a 95% confidence level.
Results

TBS

TBS (MPa) test results from Experiment 1 are summarized in Table 2. The results are classified by luting agent condition, and the data were analyzed by two-way ANOVA using the variables of CAD/CAM composite resin block (ES or HC) and elapsed time after air abrasion (D0 or D7). TBS was significantly higher for the ES blocks than for the HC blocks in the LC + RLU, CC + ESC, and CC + RLU groups; however, no significant difference was seen for the LC + ESC group. Furthermore, TBS at D0 and D7 did not significantly differ in the LC + ESC, LC + RLU, or CC + RLU groups; however, TBS was higher at D0 than at D7 in the CC + ESC group.

SEM and AFM Evaluation

SEM images of the polished surface and surface after air abrasion in ES and HC are shown in Fig. 3. There was no difference between D0 and D7 in ES or HC blocks. High magnification images of polished ES blocks revealed 0.1- to 0.2-μm filler particles (Fig. 3b, d), and polished HC blocks exhibited holes within the filler particles (Fig. 3, B arrows at [f], [h]), as well as cracks at the filler-matrix interface on the surface of D0 and D7 blocks (Fig. 3, C arrows at [f], [h]). The air-abraded surfaces of both block types showed irregular surface roughness, and cracks were present at the filler-matrix interface in polished HC blocks.

Representative AFM images of the phases and topography in ES and HC blocks are shown in Fig. 4. Differences were observed in the contrast between D0 and D7 phase images. The contrast change of HC was larger than that of ES. Topographic images showed that surface uplifts at D0 had enlarged at D7 in both block types. D0 and D7 were evaluated by using peak phase (degree) and Ra (nm), which is the arithmetic mean surface roughness of the specimen in the topographic images (Table 3). In both block types, the phase value of D7 was larger than that of D0, but HC increased more than ES, and Ra decreased.

Effect of Water Absorption on TBS

To analyze the effect of water absorption on TBS, the TBS values of the CC + ESC group in Experiment 1 and those from Experiment 2 were compared (Table 4). TBS values of ES blocks were significantly higher for D0 and D7 + Vac than for D7, but there was no significant difference between D0 and D7 + Vac. TBS values of HC
blocks were significantly higher for D0 and D7 + Vac than for D7, and a significant difference was observed between D0 and D7 + Vac specimens. When compared in relation to time after air abrasion, TBS values of ES and HC blocks significantly differed at D0 and D7, but no significant difference was observed for D7 + Vac specimens.

**Discussion**

**Experiment 1**
The main adhesive forces between the luting agent and CAD/CAM composite resin block are mechanical retention, caused by the anchoring effect of the luting agent, and chemical bonding between the luting agent and inorganic filler of the CAD/CAM composite block, which is created by application of a silane coupling agent (8,19). The initial bond strength between CAD/CAM composite resin blocks and luting agents primarily results from interlocking as the adhesive penetrates air abrasion-induced irregularities and cracks on the surface (7). Dual-cure luting agents can be cured by light polymerization or chemical polymerization. Usually, light irradiation is essential for adhesion of CAD/CAM composite resin blocks (20); however, Tashiro et al. (21) reported that transmitted light intensity decreased as the block thickened under light irradiation. In clinical
settings, both light curing and chemical curing are important for initial adhesive strength, because some areas, such as adjacent faces, are not fully reached by light irradiation. Therefore, TBS was investigated under conditions of light curing and chemical curing in this experiment.

TBS values at D0 and D7 were compared because TBS might differ when setting is performed immediately after as compared with some time following air abrasion, as is the case when air abrasion is performed at a laboratory. The null hypothesis—that the time elapsed has no effect on initial adhesive strength—was rejected because of the significant difference between D0 and D7 specimens in the CC + ESC group.

To compare the surface topographies of a CAD/CAM composite resin block under each condition, the block surfaces observed with FE-SEM and AFM. First, the difference between the polished surface of each block (Fig. 3) and the surface properties under each time condition after air abrasion (Fig. 4) observed with FE-SEM. On the polished surface, high magnification images of ES revealed nanoscale filler particles of about 0.1- to 0.2-μm, and HC exhibited various sizes of filler particles. HC blocks had cracks between the filler and matrix on the polished surface. After air abrasion, the HC surface exhibited debonding between the filler and matrix, desorption of the filler, and surface damage. However, no significant difference was observed between D0 and D7 specimens after air abrasion; thus, AFM observation was used to analyze surface properties. The probe was fixed to a 1 × 1-μm block, and fixed-point observation at D0 and D7 was performed with AFM.

In AFM dynamic mode, nanoscale properties of materials can be characterized quantitatively, and the topography of the material surface can be evaluated by analyzing the interaction between the tip and specimen (22). In ES and HC blocks, the peak phase contrast value increased from D0 to D7, and the increase was greater for HC (Table 3). The phase shifts as the AFM probe interacts with the specimen, as displayed in the phase image. Tamayo et al. (23) reported that the viscoelasticity of the specimen surface is an important cause for the phase contrast on a soft material such as a polymer; the higher the viscosity and lower the elastic modulus, the greater the phase shift. The present findings showed that the viscosity of the block surface increased with advancing time, because the peak phase value at D7 was higher than that at D0. Ra was lower at D0 than at D7 in both the ES and HC blocks. All polymer composites absorb water molecules when exposed to moist air or water immersion (24), both in the matrix phase and at the filler-matrix interface (12-14). The absorbed water causes matrix softening and swelling, as well as microcracks, resin deterioration, and debonding of the filler-matrix interface (12-14,25,26). This, in turn, affects bond strength (11).

The initial bond strength of CAD/CAM composite resin blocks and luting agents is likely attributable to mechanical retention caused by the anchoring effect of the luting agent (7); thus, it is important to promote luting agent curing. To determine if elapsed time after air abrasion has an effect on any type of luting agent, the present study used two representative types of luting agents, which differ with respect to the polymerization reaction of primer and luting agent. The primer UP used in the CC + ESC group does not contain components that promote luting agent curing and has no polymerization effect itself (Table 1). Therefore, the polymerization rate of this luting agent would be lower than that of the other groups. SEM showed many cracks at the filler-matrix interface after air abrasion in HC. Because of peeling at the filler-matrix interface, the CAD/CAM composite resin block was more likely to absorb water after air abrasion (Fig. 3). Furthermore, water molecules are most likely to accumulate at the filler-matrix interface (15), which suggests that moisture absorbed in the peeled part further inhibited polymerization of the hydrophobic luting agent, which originally had a low polymerization rate in the CC + ESC group. More water would be absorbed in the filler-matrix interface in HC than in ES, because peeling at the filler-matrix interface was more frequent in HC. This likely contributed to the significant difference in TBS between these block types.

The significant differences between the ES and HC CAD/CAM composite resin blocks, not only in the CC + ESC group but in many other groups, could be attributable to differences in the effectiveness of the silane coupling agent. Yoshihara et al. (7) found that bond strengths of CAD/CAM composite resin blocks were significantly higher after both air abrasion and silane treatment than after air abrasion only, except for HC blocks. Because of differences in filler components (28) and filler content rates, the effect of the silane coupling agent on bond strength would be greater for ES than for HC. However, the relationship between the chemical bonding of the silane coupling agent and initial bond strength remains to be investigated.
Regarding time conditions, no significant difference was found between D0 and D7 specimens for the LC condition for either luting agent, or in the CC + RLU group. As compared with the chemical-cured luting agent, the light-cured luting agent has a higher polymerization rate and better mechanical properties (21, 29). Past and present findings are consistent: TBS was significantly higher in the LC group than in the CC group. In the CC group, the chemical polymerization initiator in the luting agent is taken in by contact between the pretreatment agent Scotchbond Universal Adhesive (SB: 3M ESPE) with the RLU, and SB penetrating the block is itself also cured. RLU may thus have a high luting agent polymerization rate even when chemically cured. There was no significant difference between D0 and D7 in the LC group or CC + RLU group, for which the polymerization of the luting agent was reliable. Therefore, under the present conditions, elapsed time after air abrasion had no effect on TBS of the bond between the CAD/CAM composite resin blocks and luting agents.

**Experiment 2**

In Experiment 1, a significant difference in TBS between D0 and D7 was observed only in the CC + ESC group, which was attributed to water absorption of the block. Therefore, Experiment 2 focused on the CC + ESC group. D7 blocks were vacuum dried to determine whether water absorption of the block during the interval after air abrasion inhibited adhesion. TBS was significantly higher in the D7 + Vac group than in the D7 group, for both blocks, which suggests that removal of absorbed water by vacuum drying influenced TBS recovery. There was no significant difference between D0 and D7 + Vac in ES, but D0 and D7 + Vac significantly differed in HC. Kawaguchi et al. (2) reported that ultrasonic cleaning after air abrasion resulted in residual moisture on the block surface and reduced polymerization of the adhesive luting agent. The present discrepancy in the findings for ES and HC is therefore likely attributable to moisture retention after ultrasonic cleaning of HC after air abrasion.

The significant difference between D0 and D7 + Vac was larger in HC than in ES, because of the susceptibility of HC to cracking and filler removal by air abrasion (5), as well as the effect of moisture residue caused by ultrasonic cleaning after air abrasion. HC was more influenced than ES by moisture residue from ultrasonic cleaning after air abrasion and by water absorption during the interval from air abrasion until adhesion.

This experiment evaluated the effect of time elapsed after air abrasion on the initial bond strength of a CAD/CAM composite resin block. It should be noted that the present study is limited by the fact that the actual amount of water absorption cannot be measured. Further, it is also necessary to measure the TBS of the other conditions in Experiment 2 to determine how they are affected by water absorption. The relationship between the silane coupling agent and the initial bond strength, and the long-term durability of the luting agent using after thermal cycling should be clarified.

The present findings suggest that air-abraded CAD/CAM composite resin blocks swell because they absorb moisture in air over time, which could influence the effect of a silane coupling agent. In addition, because of differences in block characteristics, HC appeared to be more susceptible than ES to water absorption. Thus, air abrasion should be performed immediately before the bonding procedure.

**Acknowledgement**

This research was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society the Promotion of Science (No. 16K11645).

**Conflict of Interest**

The authors declare no conflict of interest.

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