Abstract: We investigated the chemical interaction between zirconia surfaces and functional monomers using X-ray photoelectron spectroscopy (XPS). Two types of zirconia disks cleaned with piranha solution were treated with one of two phosphate primers (Alloy Primer, Clearfil Ceramic Primer) or a carboxylic primer (Super-Bond C&B Monomer), and rinsed 3 times with acetone. XPS analysis revealed that phosphorus was incorporated into zirconia when the surface was treated with a primer containing phosphate monomer (10-methacryloyloxydecyl dihydrogen phosphate; MDP). However, the S 2p peak of a triazine dithiol monomer (6-[N-(4-vinylbenzyl)-n-propylamino]-1,3,5-triazine-2,4-dithione; VTD) and Si 2p peak of silane (3-trimethoxysilylpropyl methacrylate; TMSPMA) were not detected in the spectra of the primed surface. The [C]/[Zr] ratio for the surface treated with a carboxylic anhydride (4-methacryloyloxyethyl trimellitate anhydride; 4-META) primer was smaller than that treated with MDP. These results demonstrated that 4-META and MDP adsorbed to zirconia, whereas the VTD and TMSPMA did not.

Keywords: chemical bonding; functional monomer; primer; XPS; zirconia.

Introduction
Zirconia materials have been applied widely to dental restorations because they have an esthetically appealing color, high flexural strength, long-term stability, and good biocompatibility. The clinical success of high-strength ceramics, such as zirconia ceramics, depends largely on adhesion to natural teeth, alloy, and other dental materials (1). Therefore, many studies have investigated the adhesive strength of zirconia ceramics. Unlike silica-based ceramics, where hydrofluoric acid etching followed by silane treatment is effective for adhesion (2), high-strength ceramics, such as alumina and zirconia ceramics, contain acid-resistant and silica-free surfaces and require different treatments to achieve strong and durable bonds.

Micromechanical interlocking and chemical bonding are necessary for adhesion with zirconia ceramics, similar to other materials. For micromechanical interlocking, zirconia ceramics are not etched easily with hydrofluoric acid. However, air-particle abrasion with alumina before cementation was found to provide higher bond strengths for zirconia ceramics (3-5). In chemical bonding, an
acidic functional monomer, such as carboxylic anhydride (4-methacryloyloxyethyl trimellitate anhydride; 4-META) or phosphonic acid (6-methacryloxyhexyl phosphonoacetate; 6-MHPA), particularly a phosphate-based monomer (10-methacryloyloxydecyl dihydrogen phosphate; MDP), is effective for zirconia ceramics (3,6-8). Moreover, the effectiveness of silica coating and silane (3-trimethoxysilylpropyl methacrylate; TMSPMA) combination treatment or MDP and triazine dithiol monomer (6-[N-(4-vinylbenzyl)-n-propylamino]-1,3,5-triazine-2,4-dithione; VTD) combination treatment has been reported (9,10). However, previous studies performed mechanical evaluations based on bond strength data, which may include factors unrelated to chemical adhesion, such as alumina blasting.

Therefore, bond strength evaluations alone are insufficient to reveal the effect of bonding agents on zirconia ceramics. Several techniques used in materials science and surface science to analyze the composition of solid surfaces can be used to determine the elemental composition, and studies using such techniques have been reported (11-14). However, although many bond strength studies focused on bonding of zirconia ceramics have been performed under a variety of test and aging conditions, limited evidence is available on the chemical reaction between functional monomers and zirconia surfaces (15,16). We investigated chemical bonding between zirconia surfaces and functional monomers using X-ray photoelectron spectroscopy (XPS).

**Materials and Methods**

**Materials used**

Two kinds of zirconia and three kinds of primers were used in this study (Table 1). Yttria-partially stabilized tetragonal zirconia polycrystal (Y-TZP; Cercon Base; Dentsply International, Inc., York, PA, USA) and ceria-partially stabilized zirconia/alumina nanocomposite (Ce-TZP/A; Panasonic Healthcare Co., Ltd., Tokyo, Japan) were selected as zirconia materials. For the primers, two phosphate primers (Alloy Primer, AP; Clearfil Ceramic Primer (CP); Super-Bond C&B Monomer (SBM)) were used, and the main compositions of the functional monomers are listed in Table 1 and shown in Fig. 1.

<table>
<thead>
<tr>
<th>Materials/Trade name (Abbr.)</th>
<th>Main composition</th>
<th>Manufacturer</th>
<th>Batch No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia</td>
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<tr>
<td>Cercon Base (Y-TZP)</td>
<td>ZrO₂, Y₂O₃</td>
<td>Dentsply International Inc., York, PA, USA</td>
<td>18005869</td>
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<tr>
<td>P-Nano ZR (Ce-TZP/A)</td>
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<td>G222222</td>
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<td>Primer</td>
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<td>Alloy Primer (AP)</td>
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<td>Kuraray Noritake Dental Inc., Tokyo, Japan</td>
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<td>Clearfil Ceramic Primer (CP)</td>
<td>MDP, TMSPMA, ethanol</td>
<td>Kuraray Noritake Dental Inc.</td>
<td>0019BA</td>
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<tr>
<td>Super-Bond C&amp;B Monomer (SBM)</td>
<td>4-META, MMA</td>
<td>Sun Medical, Moriyama Co., Ltd., Japan</td>
<td>EV2</td>
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MDP: 10-methacryloyloxetyl dihydrogen phosphate; VTD: 6-[N-(4-vinylbenzyl)-n-propylamino]-1,3,5-triazine-2,4-dithione; TMSPMA: 3-trimethoxysilylpropyl methacrylate; 4-META: 4-methacryloyloxyethyl trimellitate anhydride; MMA, methyl methacrylate.

aAccording to information provided by the manufacturers.
Clearfil Ceramic Primer, CP, Kuraray Noritake Dental Inc., Tokyo, Japan) and a carboxylic primer (Super-Bond C&B Monomer, SBM; Sun Medical Co., Ltd., Moriyama, Japan) were used. Figure 1 shows the structural formula for the functional monomers included in each primer.

Surface preparation
Zirconia disk-shaped specimens (10 mm in diameter and 2.5 mm thick) were prepared using computer-aided design/computer-aided manufacturing (CAD/CAM) systems. All specimens were ground flat with diamond wheels (#325) and cleaned with distilled water for 10 min in an ultrasonic bath. Next, zirconia specimens were immersed in piranha solution (mixture of 14 mL concentrated sulfuric acid and 6 mL 30% hydrogen peroxide solution) for 15 min to remove the contamination layer of the specimen surface and washed with distilled water 3 times. As a control group (CO), untreated zirconia specimens were kept in acetone until just before surface analysis to prevent surface contamination. In other groups, one drop of each primer was dropped onto the zirconia surface and dried completely at room temperature. After drying, zirconia surfaces were washed with acetone 3 times to remove excess primer that did not adhere to the zirconia surface, and kept in acetone until surface analysis.

XPS analysis
Specimen surfaces were analyzed chemically using an XPS instrument (AXIS-HS; Kratos Analytical Ltd., Manchester, UK). Measurements were performed in vacuo ($\leq 10^{-7}$ Pa) with Al-Kα monochromatic X-rays at a source power of 150 W. Charge compensation was achieved with an electron flood gun equipped with the AXIS-HS instrument. Wide- and narrow-scan spectra (Zr 3p, O 1s, P 2p, S 2p, Si 2p, C 1s, Al 2s, Y 3p, Hf 4d, Ce 3d) were acquired at pass energies of 40 eV and a photoelectric uptake angle of 90°. Peak positions were calibrated by referencing a value of 285 eV in the C 1s spectrum. Quantitative data were obtained from peak areas. Reproducibility was guaranteed by taking five measurements of three specimens per experimental variable.

Statistical analysis
Quantitative data were compared by two-way analysis of variance after Levene’s test to evaluate equality of variance. The values of each primer group for each zirconia material then were compared by nonparametric Kruskal-Wallis analyses. Post hoc analysis was done with Mann-Whitney U tests performed on each pairing and applying a Ryan correction onto the P values to identify the treatments that significantly differed from each other. Differences in atomic ratios of [C]/[Zr] between Y-TZP and Ce-TZP/A for the same primer group were analyzed by the Mann-Whitney U test. All analyses were performed using IBM SPSS 22.0 (IBM Japan, Ltd., Tokyo, Japan). P values less than 0.05 were considered statistically significant.

Results
Effect of AP
AP includes two kinds of MDP for base metal alloys and VTD for noble metal alloys as a functional monomer. Because MDP contains a phosphate group in its structure, P 2p spectrum analysis was performed as an index to confirm adsorption. Figure 2 shows XPS narrow-scan spectra of the P 2p region of Y-TZP and Ce-TZP/A treated with AP. A P 2p peak was observed at an expected binding energy of approximately 129 eV in only AP with
both zirconia materials. For VTD, because it contains a mercapto group in its structure, S 2p spectrum analysis was performed as an index to confirm adsorption. An S 2p peak in XPS narrow-scan spectra was not observed at the expected binding energy of 162 eV in AP and CO with both zirconia materials (Fig. 3). Atomic ratios of [C]/[Zr] analyzed from narrow-scan spectra of C 1s and Zr 3p were 1.45 in Y-TZP and 1.81 in Ce-TZP/A, respectively (Table 2).

Effect of Clearfil CP
CP includes MDP for base metal alloys as a functional monomer and TMSPMA as a silane coupling agent. In MDP, P 2p spectrum analysis was performed as an index to confirm adsorption, as described above for AP. Figure 4 shows XPS narrow-scan spectra of the P 2p region of Y-TZP and Ce-TZP/A treated with CP. A P 2p peak was observed near an expected binding energy of 129 eV in only CP. For TMSPMA, because it contains a silicon element in its structure, Si 2p spectrum analysis was performed as an index to confirm adsorption. The expected Si 2p peak in XPS narrow-scan spectra was not observed near the binding energy of 99 eV for CP and CO with both zirconia materials (Fig. 5). Atomic ratios of [C]/[Zr] analyzed from narrow-scan spectra of C 1s and Zr 3p were 1.39 in Y-TZP and 2.08 in Ce-TZP/A, respectively (Table 2).

Effect of SBM
SBM includes 4-META as a functional monomer. Because 4-META comprises only carbon, oxygen, and hydrogen atoms, a specific elemental peak cannot be used as an index to confirm adsorption. Therefore, atomic ratios of [C]/[Zr] analyzed from narrow-scan spectra of C 1s and Zr 3p were determined, and the adsorption of 4-META was calculated by the ratio compared with those for CO,
and CP. In addition, the form of the C 1s peak was considered to indicate standard of evaluation because 4-META contains four -COO− bonds.

The intensity of the C 1s peak at a binding energy of 288.5 eV, indicating a -COO− bond, tended to be greater in SMB than CO with both zirconia materials (Fig. 6). In addition, the atomic ratios of [C]/[Zr] in SMB were 1.05 in Y-TZP and 1.48 in Ce-TZP/A, respectively. This value was significantly higher than that for CO, but similar or smaller than the two primers containing MDP (AP and CP). Furthermore, all primer groups showed significantly smaller ratios with Y-TZP than with Ce-TZP/A (Table 2).

### Discussion

Many studies have investigated adhesion of primer components to zirconia materials. However, most studies conducted mechanical evaluations based on bond strength data, which may include other factors unrelated to chemical adhesion, such as alumina blasting. Therefore, analysis of adsorbed primer components provides

### Table 2

<table>
<thead>
<tr>
<th>Y-TZP</th>
<th>CO</th>
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<th>CP</th>
<th>SBM</th>
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<tbody>
<tr>
<td>Mean</td>
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<td>1.45</td>
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<tr>
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<table>
<thead>
<tr>
<th>Ce-TZP/A</th>
<th>CO</th>
<th>AP</th>
<th>CP</th>
<th>SBM</th>
</tr>
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<tbody>
<tr>
<td>Mean</td>
<td>1.01</td>
<td>1.81</td>
<td>2.08</td>
<td>1.48</td>
</tr>
<tr>
<td>SD</td>
<td>0.09</td>
<td>0.28</td>
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<td>b, c</td>
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<td>b</td>
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</table>

**Identical letters indicate a nonsignificant difference (P > 0.05, Mann-Whitney U test with Ryan correction).**

**“S” indicates that the difference between Y-TZP and Ce-TZP is significant (P < 0.05, Mann-Whitney U test).**
important information on the bonding mechanisms involved.

MDP currently is the most widely used functional monomer and is effective for dental hard tissues, base-metal alloys, and polycrystalline ceramics, such as alumina and zirconia. It is reported that chemical bonding occurs through the phosphate group contained in MDP. Chen et al. (15) reported that mass spectrometry fragment patterns indicated the existence of P-O-Zr formation on zirconia surfaces primed with a zirconia primer containing a phosphate monomer. In our study, P 2p peaks in XPS narrow-scan spectra were recognized near a binding energy of 129 eV in AP and CP with both zirconia materials (Figs. 2, 4). This finding revealed that MDP chemically adhered to zirconia surfaces. Conversely, an S 2p peak (indicating the existence of VTD) was not observed near the expected binding energy of 162 eV in AP with both zirconia materials (Fig. 3). MDP in AP is adsorbed on base metal alloys, whereas VTD is chemisorbed mainly on gold (Au), silver (Ag), and copper (Cu) surfaces (13,14). Because zirconia is an oxide of zirconium, which is a metallic element and base metal, our findings revealed that VTD does not adhere chemically to zirconia surfaces.

TMSPMA is one of the representative silane treatment agents used in dental applications. Hydrolyzable alkoxy groups of TMSPMA react with silanol groups on silica-based ceramic surfaces to form siloxane bonds. However, silane treatment is ineffective for zirconia ceramics because zirconia ceramics contain low silica content (6). In our study, a Si 2p peak in XPS narrow-scan spectra was not detected on either zirconia material, confirming the lack of silica (Fig. 5). Therefore, surface modification, such as a tribochemical silica coating, is necessary to enhance adhesion to zirconia materials when using primers containing TMSPMA.

4-META monomer has been shown to be effective in improving bonding between base metal alloys and metal oxides by mechanical data (17). Our study used atomic ratios of [C]/[Zr] analyzed from narrow-scan spectra of C 1s and Zr 3p on specimen surfaces to evaluate adsorption of 4-META because 4-META comprises only carbon, oxygen, and hydrogen atoms. The atomic ratios of [C] of the group treated with a bonding agent including 4-META (SBM) were significantly higher than those of the untreated CO group (Table 2). In energy dispersive X-ray microanalysis, zirconia peaks on primed surfaces were masked off by adsorbed primer films, which demonstrated increased [C] and [O] intensity peaks (16). These results indicated that 4-META also chemically adheres to zirconia. However, the atomic ratios of [C] in 4-META were similar or smaller than those in the two primers group (AP and CP) containing MDP (Table 2). Considering that MDP contains fewer carbon atoms than 4-META (14 vs. 15, respectively), 4-META likely forms a chemical bond with the zirconia surface and has less adsorption than MDP (Table 2). Furthermore, in the comparison between Y-TZP and Ce-TZP/A, the atomic ratios of [C] of Ce-TZP/A were significantly higher in all groups than those in Y-TZP. Y-TZP primarily comprises ZrO2, whereas Ce-TZP/A contains 30 vol% Al2O3. This compositional difference may explain the difference in adsorption of the functional monomer.

Our study revealed that carboxylic anhydride (4-META) and phosphate monomers (MDP) adsorbed to zirconia, whereas the triazine dithiol monomer (VTD) and silane (TMSPMA) did not.

Acknowledgments
This work was supported by JSPS KAKENHI Grant Numbers JP24592916 and JP16K11593.

Conflict of interest
The authors have no conflict of interest to declare.

References


