The purpose of this study was to use a tape casting technique to develop an Al$_2$O$_3$ fiber-reinforced Al$_2$O$_3$-based ceramic material (Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite) into a new type of dental ceramic. The Al$_2$O$_3$-based ceramic used a matrix consisting of 60 wt% Al$_2$O$_3$ powder and 40 wt% SiO$_2$-B$_2$O$_3$ powder. The prepreg sheets of Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite (in which uniaxially aligned Al$_2$O$_3$ fibers were infiltrated with the Al$_2$O$_3$-based matrix) were fabricated continuously using tape casting technique with a doctor blade system. Multilayer preforms of Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite sheets were then sintered at a maximum temperature of 1000°C under an atmospheric pressure in a furnace. The results showed that the shrinkage and bending properties of Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite exceeded those of unreinforced Al$_2$O$_3$—hence demonstrating the positive effects of fiber reinforcement. In conclusion, the tape casting technique has been utilized to successfully develop a new type of dental ceramic material.

Key words: Al$_2$O$_3$ fiber-reinforced Al$_2$O$_3$-based ceramics, Sheet, Tape casting

INTRODUCTION

Dental ceramics are commonly used as esthetic restorative materials for crowns, bridges, and fixed partial dentures. Metal-ceramics have been especially popular for restorations in fixed prosthodontics. However, the metals used in metal-ceramic restorations have the potential of causing allergic or toxic reactions within the soft or hard tissues. Therefore, there is extensive clinical research on developing metal-free restorations or metal-ceramic restorations using pure titanium with a high degree of biocompatibility. Moreover, it is well known that metal-free restorations provide an aesthetic promise unmatched by conventional metal-ceramic restorations. This is because metal-ceramic materials are known to cause graying of the gingival margin due to metal show-through.

Against this backdrop of heightened use of ceramics for restorative procedures and the constant demand for improved clinical performance, several new ceramic restorative materials and techniques have been developed to-date. For example, various kinds of new ceramics such as castable ceramics and CAD/CAM ceramics, which have been introduced into dentistry since the 1980s have shown considerable potential as restorative materials. These new dental ceramic materials offer higher degrees of esthetics and biocompatibility than do those of conventional porcelain ceramics and metal-ceramics. However, restorations made of these materials are not as strong as those that are supported with metal because of their intrinsic mechanical properties.

To overcome the above-mentioned problems, concerted efforts and detailed studies have been devoted to developing fiber-reinforced composite materials—the achievements of which have become a center of attention in dentistry. It has been demonstrated through researches (including clinical experiments) that it is possible to use fiber-reinforced composites in dental appliances such as crowns, bridges, and frameworks for fixed partial dentures.

Currently, one industrial method that is used to manufacture flat ceramics with precise thickness control and consistency is the tape casting technique. This method employs specially formulated ceramic slurry, which is cast by a doctor blade onto a flat sheet or carrier, and then dried on a green sheet. A key advantage of the tape casting technique is that the thickness of the films can be precisely controlled by adjusting the gap of the blades with a micrometer screw gauge. Armed with precision and consistency, tape casting products have found their applications in a wide variety of industries, such as microelectronics, photovoltaic solar applications, laminated composites, and rapid prototyping. In dentistry, ceramic sheets can be potentially utilized in a wide range of dental applications, such as crowns, bridges, laminate veneers, cooping, as dental ceramics for many types of restoration in fixed prosthodontics and also as traditional dental ceramics.

Hinging on the vast potential of fiber-reinforced ceramic sheets in dental applications, the purpose of this study was to use the tape casting technique to develop an Al$_2$O$_3$ fiber-reinforced Al$_2$O$_3$-based ceramic material (Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite) into a new type of dental ceramic material.
type of dental ceramic.

MATERIALS AND METHODS

Fabrication of Al₂O₃-fiber/Al₂O₃ composite

Fig. 1 is a flowchart of the fabrication process of Al₂O₃-fiber/Al₂O₃ composite. An Al₂O₃-based powder, consisting of 60 wt% Al₂O₃ powder (α-Al₂O₃, AL45-1, Showa Denko Co. Ltd., Tokyo, Japan) and 40 wt% SiO₂-B₂O₃ glass powder (SNK-01, Senyo Glass Co. Ltd., Osaka, Japan) with compositions (wt%) of 33 SiO₂, 32 B₂O₃, 20 CaO, and 15 MgO, was used as a matrix for the Al₂O₃-fiber/Al₂O₃ composite (Fig. 2).

First, an Al₂O₃-based aqueous slurry was prepared by mixing 18 g Al₂O₃ powder, 12 g SiO₂-B₂O₃ powder, 0.12 g copolymer of acrylic acid and acrylic acid ester (AQ-2559, Lion Co., Tokyo, Japan) as dispersant, 6 g distilled water (Wako Pure Chem. Ind. Ltd., Osaka, Japan), and 6 g ethanol (Wako Pure Chem. Ind. Ltd., Osaka, Japan) in an Al₂O₃ container with two different sizes of Al₂O₃ balls (ϕ = 3, 5 mm) for 18 hours with a planetary ball mill (P5/2, Fritsch Japan Co. Ltd., Kanagawa, Japan). Next, 4.8 g copolymer of acrylic acid and acrylic acid ester (HB-500, Lion Co., Tokyo, Japan) as binder, 0.6 g polyethylene glycol (PEG # 600, Lion Co., Tokyo, Japan) as plasticizer, 0.03 g n-alkyl alcohol (1020H, Lion Co., Tokyo, Japan) as dispersing agent, 0.06 g ammonia water (25% ammonia solution, Wako Pure Chem. Ind. Ltd., Osaka, Japan), and 1.5 g ethanol were added to the initially prepared Al₂O₃ slurry and further mixed by ball milling for 2 hours. Finally, the Al₂O₃ slurry was degassed using a rotary pump for 30 minutes.

The reinforcement used was Al₂O₃ fiber (γ-Al₂O₃, Alflex, Taimei Chem. Co. Ltd., Nagano, Japan) with a mean diameter of 10 μm (Fig. 3). The prepreg sheets of Al₂O₃-fiber/Al₂O₃ composite (in which the uniaxially aligned Al₂O₃ fibers were infiltrated with the Al₂O₃ matrix) were fabricated continuously by a doctor blade system (DP-150, Sayama Riken Corp., Saitama, Japan), as shown in Fig. 4. Here, the Al₂O₃ fibers were fixed to a carrier film, which moved at a speed of 20 cm/min, so that the Al₂O₃ fibers became impregnated by running through the Al₂O₃-based slurry. The heights of blades A and B were adjusted to 1.0 mm and 1.5 mm respectively. The width of the Al₂O₃-fiber/Al₂O₃ composite sheet was 150 mm, whereby this width is limited only by the size of the doctor blade machine. The sheet was then dried at room temperature to remove the solvents. A digital micrometer was used to measure the thickness of the Al₂O₃-fiber/Al₂O₃ composite sheet at varying locations on the cast tape. Monolayer pieces were then cut into specimen geometry, laminated, and pressed together to prepare multilayer preforms. Then, before sintering, 5 plies of the Al₂O₃-fiber/Al₂O₃ composite sheets were stacked and pressed.
Fig. 4 Schematic illustration of tape casting process for Al₂O₃-fiber/Al₂O₃ composite sheet fabrication.

... under a pressure of 21 MPa. Finally, the multilayer preforms of the Al₂O₃-fiber/Al₂O₃ composite sheets were sintered at a maximum temperature of 1000°C under an atmospheric pressure for 4 hours in a furnace (MSPT-1520-P, Nikkato Corp., Tokyo, Japan). After sintering, Al₂O₃-fiber/Al₂O₃ composite samples with a fiber content of about 6 vol% were obtained. Apart from the reinforced specimens, an unreinforced Al₂O₃ sample was prepared so that it could serve as control while the effects of fiber reinforcement were being investigated.

Particle size analysis
To confirm the effectiveness of ball milling for the Al₂O₃-based slurry, particle size distribution of the Al₂O₃-based slurry was measured using a laser diffraction particle size analyzer (SALD-7000, Shimazu Corp., Kyoto, Japan). All adjustable measurement parameters – such as flow rate through optical cell, stirrer speed, and ultrasonics – were kept constant at the same level for all samples. The mean particle size was defined as half of the cumulative volume.

Observation by field-emission scanning electron microscopy
After vacuum-drying and platinum-sputtering of the specimen surface, the surface appearance of the Al₂O₃-fiber/Al₂O₃ composite was observed with a field-emission scanning electron microscope (FE-SEM, JSM-6340F, JEOL, Tokyo, Japan) at an acceleration voltage of 5 kV.

X-ray diffraction
The developed Al₂O₃-fiber/Al₂O₃ composite was characterized by X-ray diffraction (XRD, θ-2θ diffractometer, Geigerflex, Rigaku Corp., Tokyo, Japan), which had an X-ray source of Cu Kα and a power of 40 kV × 30 mA. Samples were placed in an aluminum holder. All collected X-ray spectra were corrected by using pure silicon (99.99%) as an external standard.

Sintering shrinkage measurement
The specimens used for measuring sintering shrinkage were plates measuring 25-mm long (X-axis), 15-mm wide (Y-axis), and 2-mm thick (Z-axis). The unidirectional fiber orientation was the X-axis. Before and after sintering, the length of the side of each specimen was measured by a digital micrometer. The linear shrinkage \( L_s \) along the X-, Y-, and Z-axes, and the volume shrinkage \( V_s \) were then calculated from the following equations:

\[
L_s(\%) = \frac{(L_b - L_a)}{L_b} \times 100 \quad (1)
\]

\[
V_s(\%) = \frac{(V_b - V_a)}{V_b} \times 100 \quad (2)
\]

where \( L_a \) is the length of the sample before sintering, \( L_b \) is the length of the sample after sintering, \( V_a \) is the volume of the sample before sintering, and \( V_b \) is the volume of the sample after sintering. The experimental values are the average of five measurements (n=5).

Three-point bending test
The specimens used for bending test were rectangular bars measuring 18-mm long, 4-mm wide, and 3-mm thick. Three-point bending tests were performed at a constant loading speed of 0.5 mm/min at a span length of 16 mm by use of a computer-controlled Instron testing machine (TCM500CR, Minebea, Tokyo, Japan). The bending strength \( F \) and bending modulus \( E \) were calculated from the following formulas:

\[
F = \frac{(3/2)(PL/bh^2)}{1} \quad (3)
\]

\[
E = \frac{(1/4)(L^3/bh^3)k}{1} \quad (4)
\]

where \( P \) is the maximum load, \( L \) is the span length, \( b \) is the specimen width, \( h \) is the specimen thickness, and \( k \) is the slope at the initial stage in the load-deflection curve. The experimental values are the average of 12 measurements (n=12). In addition, the continuous fiber is oriented in the longitudinal direction.

Statistical analysis of data
The data were examined with an analysis of variance (ANOVA) and tested by Scheffe's multiple comparisons test among the means at \( p=0.05 \).

RESULTS
The particle size distribution of the Al₂O₃-based powder before ball milling, and that of the slurry after the first and second ball milling steps are presented in Fig. 5. Before ball milling, the Al₂O₃-based powder had a wide distribution of diameters in the range of 0.1 µm to 100 µm, and the mean particle size was 7.86 µm, as depicted in Fig. 5(a). After 18 hours of ball milling (first slurry), the size distribution of the Al₂O₃-based powder in the slurry was not as large and the mean particle size was 3.65 µm (Fig. 5(b)). In the second slurry, the mean particle size of the Al₂O₃-based powder was reduced to 3.27 µm (Fig. 5(c)).

Fig. 6 shows an Al₂O₃-fiber/Al₂O₃ composite sheet fabricated in this study. The thickness of the sheet was about 1.0 mm. Fig. 7 is an FE-SEM image of...
this composite sheet, which confirms that the Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite sheet is composed of Al$_2$O$_3$ fibers and Al$_2$O$_3$-based powder. Fig. 8 is an FE-SEM image of the surface of Al$_2$O$_3$-fiber/Al$_2$O$_3$ composite after sintering at 1000°C. Fig. 8 confirms that no Al$_2$O$_3$ powder remained on the surface and that the surface was smooth. In addition, the Al$_2$O$_3$-fiber/
Al₂O₃ composite was densely sintered at the sintering temperature of 1000°C. Fig. 9 shows the XRD spectra of the Al₂O₃-fiber/Al₂O₃ composite sheet and the Al₂O₃-fiber/Al₂O₃ composite after sintering at 1000°C. The spectra of the Al₂O₃-fiber/Al₂O₃ composite sheet confirmed the typical Al₂O₃ peaks at 2-theta values of 25.62, 35.20, 37.82, 43.40, 52.57, 57.53, 61.35, 66.53, and 68.22 degrees. In contrast, the spectra of Al₂O₃-fiber/Al₂O₃ composite after sintering at 1000°C had 3Al₂O₃-2SiO₂ peaks at 2-theta values of 16.72, 26.58, 33.70, 36.90, and 41.80 degrees, and SiO₂ (cristobalite) peaks at 2-theta values of 22.02, 28.08, and 36.05 degrees (in addition to the typical Al₂O₃ peaks at 2-theta values of 25.63, 35.20, 37.82, 43.40, 52.58, 57.53, 61.33, 66.55, and 68.23 degrees).

Table 1 shows the linear shrinkage and volume shrinkage of Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃ after sintering. There were significant differences in the linear shrinkage of the X- and Z-axes between Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃ (p<0.05). Also, there was significant difference in the volume shrinkage between Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃ (p<0.05).

Table 2 shows the bending properties of both Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃ obtained from three-point bending test. There were significant differences in both the bending strength and bending modulus between Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃ (p<0.05). Fig. 10 shows FE-SEM images of the fracture surfaces of Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃ after the three-point bending test. The FE-SEM image of the fractured Al₂O₃-fiber/Al₂O₃ composite revealed a reactive layer between the fiber and matrix. Moreover, the fibers were bunched up in the matrix (Fig. 10(a)). In contrast, the fracture surface of Al₂O₃ was smooth (Fig. 10(b)).

**DISCUSSION**

In the present study, we used a tape casting technique to develop an Al₂O₃ fiber-reinforced Al₂O₃-based ceramic material (Al₂O₃-fiber/Al₂O₃ composite) into a new type of dental ceramic. The tape casting technique can be easily employed as a fast and non-energy consuming procedure to mass produce ceramic sheets with good uniformity and reproducible properties. Intrinsically, Al₂O₃ — which is used as a ceramic material — is a hydrophilic, low-friction, thermodynamically and chemically stable material. Moreover, in this study, SiO₂-B₂O₃ powder was added to the Al₂O₃ powder to lower the sintering temperature to avoid degradation of the Al₂O₃ fibers during sintering.

### Table 1 Sintering shrinkages of Al₂O₃-fiber/Al₂O₃ composite and Al₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear shrinkage (X-axis (%))</th>
<th>Linear shrinkage (Y-axis (%))</th>
<th>Linear shrinkage (Z-axis (%))</th>
<th>Volume shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃-fiber/Al₂O₃ composite</td>
<td>1.52±0.63</td>
<td>6.21±0.80</td>
<td>5.12±3.51</td>
<td>12.34±4.04</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.21±1.04</td>
<td>7.02±1.53</td>
<td>16.19±3.59</td>
<td>27.68±3.65</td>
</tr>
</tbody>
</table>

Each experimental value (mean±standard deviation) is the average of five measurements (n=5). Values connected by vertical bars are significantly different from each other (p<0.05).
Table 2  Bending properties of $\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite and $\text{Al}_2\text{O}_3$

<table>
<thead>
<tr>
<th>Material</th>
<th>Bending Strength (MPa)</th>
<th>Bending Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite</td>
<td>179.6±13.0</td>
<td>31.4±4.1</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>145.3±24.5</td>
<td>19.8±2.6</td>
</tr>
</tbody>
</table>

Each experimental values (mean ± standard deviation) is the average of 12 measurements ($n=12$)
Values connected by vertical bars are significantly different from each other ($p<0.05$)

Use of the tape casting technique to prepare the $\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite sheet requires control of the size distribution of the original powder. In the present study, ball milling was performed to achieve this control. The $\text{Al}_2\text{O}_3$-based powder had two different particle sizes (Fig. 5). A preliminary measurement revealed that the mean particle sizes of $\text{Al}_2\text{O}_3$ powder and $\text{SiO}_2$-$\text{B}_2\text{O}_3$ powder were 1.89 $\mu$m and 42.10 $\mu$m respectively. Two steps of ball milling produced the appropriate particle size for tape casting. The first step of ball milling was used to better disperse the $\text{Al}_2\text{O}_3$-based powder; the second step was used to furnish better forming ability and to improve the handling properties of the $\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite sheet. While preparing the flat ceramic sheets, it was necessary to add a dispersant in the first slurry, and a binder and plasticizer in the second slurry. The dispersant used in the first slurry consisted mostly of copolymer of acrylic acid and acrylic acid ester. In the second slurry, the binder consisted mostly of copolymer of acrylic acid and acrylic acid ester while the plasticizer consisted mostly of polyethylene glycol.

The major advantage of the tape casting technique is that the thickness of the ceramic sheet can be adjusted precisely simply by varying the gap between the blades and the glass surface. Moreover, tapes with large lateral dimensions can be cast (see Fig. 4). In the present study, the thickness of the prepared $\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite sheet was about 1.0 mm, which closely corresponded with the difference in the heights of blades A and B. As a result, the multi-filament $\text{Al}_2\text{O}_3$ fibers were well infiltrated into the $\text{Al}_2\text{O}_3$-based slurry in the doctor blade system. Fig. 7 shows a tight binding between the $\text{Al}_2\text{O}_3$-based powder and $\text{Al}_2\text{O}_3$ fiber in the $\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite sheet. Furthermore, the XRD spectra of the $\text{Al}_2\text{O}_3$-fiber/$\text{Al}_2\text{O}_3$ composite sheet revealed that the crystallographic structure was the same as that of the original $\text{Al}_2\text{O}_3$ powder. These results indicate that tape casting technique produced sheets with good uniformity and with properties closely resembling those of the original powder.
materials. Conversely, the XRD spectra of the Al₂O₃-fiber/Al₂O₃ composite after sintering at 1000°C had the peaks of 3Al₂O₃·2SiO₂ and SiO₂ (cristobalite) in addition to the typical Al₂O₃ peaks. This indicates that SiO₂-B₂O₃ had been transformed after sintering at 1000°C because Al₂O₃-based ceramics contains SiO₂-B₂O₃. Fig. 8 shows that the Al₂O₃-fiber/Al₂O₃ composite was densely sintered at a temperature of 1000°C.

Currently, there are a few reports about fiber-reinforced laminated ceramics. For example, Yoshida et al. prepared hot-pressed, silicon carbide fiber-reinforced silicon carbide laminated composites. Hirata et al. prepared Si-Ti-C-O fiber-reinforced mullite laminated composites. However, their laminated composites were fabricated under a pressure of 40 MPa and at a higher sintering temperature of 1500-1750°C. In contrast, in this study, laminated Al₂O₃-fiber/Al₂O₃ composite was fabricated under pressureless sintering at a lower temperature of 1000°C.

The effect of the B₂O₃ powder as additives in the crystallization of ceramics has been investigated by several researchers. For promising effect in crystallizing the matrix phase and reducing the sintering temperature (to avoid thermal degradation of Al₂O₃ fibers), SiO₂-B₂O₃ powder was added to Al₂O₃ powder in the present study. For tape casting technique to be successfully utilized in dental applications, lowered sintering temperatures and pressureless sintering are important factors because expensive fabrication facilities are not required.

The volume shrinkage of Al₂O₃-fiber/Al₂O₃ composite was 2.3 times less than that of Al₂O₃ (Table 1). The bending strength of Al₂O₃-fiber/Al₂O₃ composite was 1.2 times greater than that of Al₂O₃. In addition, the bending modulus of Al₂O₃-fiber/Al₂O₃ composite was 1.6 times greater than that of Al₂O₃ (Table 2). These results demonstrate that the shrinkage and bending properties of Al₂O₃-fiber/Al₂O₃ composite are an improvement over unreinforced Al₂O₃, hence clearly and plainly demonstrating the benefits of fiber reinforcement.

A fiber-reinforced material contains a matrix pre-impregnated with fibers. It derives its strength from the fiber's bending modulus and strength, which are significantly greater than are those of the matrix alone. Many companies have been introducing new systems of dental materials using fibers. These materials are generally fabricated manually, and require special facilities. In other words, these systems use continuously oriented fibers pre-impregnated with monomers ready for curing with heat or light under pressure. In contrast, the Al₂O₃-fiber/Al₂O₃ composite fabricated in this study is an all-ceramic material composed of Al₂O₃-fiber reinforcement and Al₂O₃-based ceramic. Compared with other fiber systems, the fabrication process developed in this study requires no special fabrication facilities because of the low sintering temperature and pressureless sintering.

In conclusion, the Al₂O₃-fiber/Al₂O₃ composite produced in the present study has several distinct advantages. It is adaptable to various types of dental ceramic materials such as crowns, bridges, and laminate veneers because of its superior producibility and excellent mechanical properties. Potentially, tape casting is expected to become an important technique for applications in the field of dentistry. Further, the characterizations and mechanical properties of Al₂O₃-fiber/Al₂O₃ composite reflect those of ceramics or fibers other than Al₂O₃. As for sintering temperature, its influence on the technique should be further investigated.

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