INTRODUCTION

Among prosthetic polymers, polymethyl methacrylate (PMMA) resins have been recognized as the only proven materials for denture bases fabricated via compression/injection-molding and heat-curing processes1-3). However, since polyamide (nylon) was first used to fabricate denture bases in the 1950s, thermoplastic resins have attracted interest as an alternative material to PMMA for patients who cannot tolerate PMMA denture bases4,5). The major advantages of thermoplastic resins over conventional acrylic resins are their relative flexibility and non-breakable and hypoallergenic nature as well as the enhanced aesthetic appearance when used as a non-metal clasp denture6-8). Therefore, the use of thermoplastic resins in the construction of removable partial dentures with/without metal frameworks has recently increased. However, there are also disadvantages associated with these materials, including their inadequate mechanical properties, high degradation and challenges associated with polishing and repair7,8). A wide variety of thermoplastic polymers are used to fabricate dental prostheses. In addition to polyamide, thermoplastic resin materials including polyester, polycarbonate, and thermoplastic acrylates, are also classified as Type 3 denture base polymers in ISO 20795-19).

The mechanical properties of denture base materials are a major concern because clinical surveys have revealed a higher incidence rate of denture fracture during service10). Therefore, the comparative mechanical performance of dental thermoplastic resins is important to dental clinicians and researchers for choosing or developing proper denture base materials. The flexural properties are frequently selected during the mechanical evaluation of denture base resins10-12). Several studies have investigated the flexural properties of thermoplastic resins. A study by Pfeiffer et al. introduced thermoplastic denture base polymers with flexural strength comparable to heat-polymerized PMMA6). However, the flexural strength and modulus of polyamide denture base resins (Valpast, Luciton FRS) were significantly lower than that of heat-polymerized PMMA13-15) and failed to meet the minimum requirements of ISO 20795 (flexural strength of 65 MPa and flexural modulus (FM) of 2,000 MPa). Hamanaka et al. also reported relatively low flexural properties at the proportional limit (PL) point16,17). There have been other reports demonstrating higher flexural strength of thermoplastic resins18-20). Cumulatively, there are substantial differences or conflicts in the reported mechanical properties within the literature data and between the literature and manufacturer data9). As a result, further investigations of the flexural mechanical properties of thermoplastic denture base polymers using standardized methodology are warranted.

It is well known that water molecules can penetrate
a polymer structure and act as a plasticizer, resulting in the decrease of mechanical properties. Additionally, the fracture load of acrylic resin specimens tested in water is lower than that of resins tested in air. ISO 20795 specifies that flexure testing for denture base polymers should be conducted in (37±1)°C distilled water (DW) to simulate oral conditions after immersion in (37±1)°C water for 50 h. However, most previous studies performed flexure testing in air, although the specimens were immersed in water, or did not document the procedure for the test environment, thus hindering fair comparisons of mechanical properties among products using the same or different types of polymers.

The aim of this study was to investigate the flexural mechanical properties of various dental thermoplastic denture base polymers (six polyamides, four acrylates, polyester, polypropylene, and polycarbonate) in accordance with ISO 20795-1, including ultimate flexural strength (UFS) and strain, FM, PL, and the energy absorbed per unit area to the maximum flexure load of the materials. Additionally, the influence of the test environment (air vs. water) and specimen condition (dry vs. wet) were examined for the thermoplastic resin specimens using three different testing conditions: under DW after immersion in DW (ISO 20795-1, 'Wet/Water'), in ambient air after immersion in DW ('Wet/Air'), and in ambient air after desiccation for 7 days ('Dry/Air'). The null hypothesis of this investigation was that the testing conditions (Wet/Water, Wet/Air, Dry/Air) do not affect the flexural mechanical properties of the thermoplastic denture base polymers.

### MATERIALS AND METHODS

#### Specimen preparation

We analyzed 13 types of thermoplastic resin denture base materials: 6 polyamides (FV, FR, VP, LF, RN, and ST), 4 PMMA resins (AT, FA, SR, and AS), 1 polyester (ES), 1 polypropylene (UG) and 1 polycarbonate (JC) (Table 1). All thermoplastic resins were supplied in pellet form with an aluminium cartridge. The flexural specimens were prepared by an injection molding system.
Fig. 1 Testing condition under DW and determination of mechanical parameters. (A) Flexural test of thermoplastic specimen in (37±1)°C circulating water bath. (B) Typical flexural stress-strain curve of thermoplastic polymer specimens and determination of the flexural mechanical properties.

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(Success Injection System, Dentsply, PA, USA) except for the polycarbonate material due to its high melting temperature (320°C). The polycarbonate specimens were prepared by an automatic injection system (YX-IVQW, Aulen, Changsha, China). Thermoplastic polymer granules were dried in an electric oven under the recommended conditions before injection molding (Table 1). Stone molds for specimen were prepared using baseplate wax block and metal flask. The resins were then melt-injected into the metal flask preheated using heat lamps. Injection molding was conducted using the injection systems at a pressure of 7 bar for 1 min and bench-cooled. The investigated thermoplastic resins and the melting temperature for preparing the specimens are summarized in Table 1. The injected thermoplastic resin samples were machined flat and parallel using a dental diamond disk trimmer (Shinmyung, Seoul, Korea) with water cooling. Then, the specimen surfaces were finished on a polishing machine (Rotopol 5, Struers, Ballerup, Denmark) with wet-grinding SiC papers (P400-P800-P1200) to a size of 64.0×10.0±0.2×3.3±0.2 mm in accordance with ISO 20795. The final dimensions of the specimens were averaged from three measurements with an accuracy of 0.01 mm using a digital calliper. The deviations between the three measurements were within ±0.05 mm. Sample with bubbles or defects were excluded from testing.

**Determination of flexural mechanical properties**

The flexural mechanical properties were determined using a three-point bending test in accordance with ISO 20795-1. All specimens were immersed in DW at 37°C for 50±2 h prior to flexural testing. The specimens were placed symmetrically on a flexural test metal rig (4.0 mm cylindrical support) with a 50-mm span distance in a circulating water bath at (37±1)°C and the specimen was allowed to come to equilibrate with the water temperature (Fig. 1A). The central loading plunger and two test rigs were 4 mm in diameter. The flexural test was performed using a material testing machine (Instron 3344, Norwood, MA, USA) with a PC-controlled program (Bluehill 2, Instron) at a constant displacement rate of 5 mm/min. The flexural loading was continued to the peak maximum load of the specimens and stopped when the load dropped by 2 N from the maximum load using the Bluehill program (Fig. 1B).

The ultimate flexural strength (UFS, $\sigma_f$) and strain ($\varepsilon_f$) were calculated at the maximum flexure load on the load-displacement curve using the following equations:

\[ \sigma_f = \frac{3PL}{2bd^2} \]  
\[ \varepsilon_f = \frac{6dD}{L^2} \]

where $P$ is the maximum flexure load (N), $L$ is the length of the support span (50 mm), $b$ is the width of the specimen (mm), $d$ is the height of the specimen (mm), and $D$ is the deflection (mm) at the mid-span.

When specimens are highly deformed during the flexural testing by more than 10% of the supporting span, the UFS value can be reasonably corrected by the following equation according to ASTM D79010,12,25):

\[ \sigma_f = \sigma_u [1+6(D/L)^2−4(D/L)(D/L)] \]  

(3)

In this equation, $D$ and $L$ are the same as for Eqs. 1 and 2.

A modulus line was constructed along the slope of linear portion of the stress-strain curve for calculation of FM using the Bluehill program. The FM ($E$) values were calculated using the following equation:

\[ E = \frac{L^3m}{4bd^3} \]

(4)

In this equation $L$, $b$, and $d$ are the same as for Eq. 1, and $m$ is the slope of the modulus line (N/mm).

An offset line parallel to the modulus line was placed at 0.05% flexural strain. The $PL$ ($\sigma_w$) was determined at the intersection of the offset line and the flexural stress-strain curve (Fig. 1B). This method permits the determination of $PL$ value in a reliable and self-consistent manner by preventing from possible reading errors at the end of the elastic deformation range10).

The total amount of energy obtained from the area...
under the flexural load-deflection curve was divided by the cross-sectional area of the specimen to calculate the energy absorbance (EA) per unit area ($E_a$, kJ/m$^2$)\textsuperscript{10,26}. The thermoplastic resins required $E_a$ to be calculated up to the maximum load by flexure testing:

$$E_a = U/(bd)$$ \hfill (5)

In this equation, $U$ is the energy to maximum flexure (Joule, N·m), and $b$ and $d$ are the same as for Eq. 1. Six flexural specimens were tested for each resin ($n$=6).

### Influence of test conditions

To reveal the effects of test (air vs. water) and specimen condition (dry vs. wet) on flexural properties, 8 thermoplastic resins were chosen among 13 products: 3 types of polyamide (FV, VP and RN), 2 types of acrylate (AT and AS), polyester (ES), polypropylene (UG), and polycarbonate (JC). An additional twelve flexural specimens were prepared from each resin. All specimens were stored in 37°C water for 50 h prior to flexural testing. Six specimens per resin were used for the flexural test in ambient air at (23±2)°C with a relative humidity of (60±5)% immediately after removal of the surface water using tissue paper (designated as Wet/Air). The remaining six specimens were desiccated in an automatic dry cabinet (Sanplatec, Osaka, Japan) that maintained a relative humidity of approximately 30% for 7 days. The dried specimens were then tested in ambient air in the same way as the Wet/Air specimens (designated as Dry/Air). The data were compared with the results tested according to ISO 20795-1 as described (designated as Wet/Water (ISO)).

### Water sorption

The apparent water sorption of the flexural specimens was measured to examine the effect of water sorption on the flexural properties. The desiccated Dry/Air specimens for each group were weighed with an accuracy of ±0.1 mg using an analytic balance (Explorer, Ohaus, Parsippany, NJ, USA) before flexural testing (m$_1$). The specimens were immersed in 37°C DW for 50 h after testing. The specimens were then removed from the water and wiped with a clean tissue before they were re-weighed (m$_2$). The apparent water sorption ($W_{sp}$) of the specimen groups ($n$=6) was determined using the following equation: $W_{sp}$ (μg/mm$^3$) = ($m_2$ − $m_1$)/V, where V (mm$^3$) is the volume of the specimen.

### Statistical analysis

A one-way analysis of variance (ANOVA) and Scheffe’s multiple contrast post hoc tests were performed for each flexural mechanical property (PL, UFS, corrected UFS, flexural strain, FM, and EA) to compare the material groups (IBM SPSS Statistics 23, Armonk, NY, USA). A two-way ANOVA was conducted to examine the effects of the test and material variations and their interaction on the flexural properties. The effects of the test medium and specimen conditions on the flexural properties were also analyzed using ANOVA and Scheffe’s test. All $p<0.05$ values were considered statistically significant.

### RESULTS

Figure 1B shows a characteristic flexural stress-strain curve of a thermoplastic polymer sample with various mechanical parameters indicated. All of the thermoplastic resins investigated were deformed without fracture during the flexure testing. Thus, it is reasonable to calculate the flexural properties at the maximum load without continuing the flexure testing over the maximum load (Fig. 1B). First, according to ISO 20795-1 (Wet/Water (ISO)), the various flexural properties of the specimen groups were tested in a water bath at 37°C after immersion in DW at 37°C for 50 h (Table 2). The mean UFS and FM of the thermoplastic resins investigated varied from 27 to 89 MPa and from 611 to 2,245 MPa, respectively, depending on their chemical composition. There was a significant difference in the flexural properties observed even within the same material types of the composition (polyamide or thermoplastic acrylate). Specifically, the flexural mechanical properties, such as PL, UFS, and FM, of some polyamides (FV, FR, and VP) and polypropylene (UG) were significantly lower than those of the other polyamides (LF, RN, and ST) and acrylates (AT, FA, SR, and AS) ($p<0.05$). The values for the ES polyester material were similar (UFS) to or larger (FM) compared to the higher-strength polyamides (LF, RN, ST). The polycarbonate (JC) had the highest flexural strength and modulus of the thermoplastic polymers, and the difference was statistically significant ($p<0.05$). We found that the corrected UFS values obtained from Eq. 3 were significantly increased relative to their respective uncorrected UFS values (4 to 25%) (Table 2).

Table 3 displays the results of two-way ANOVA indicating that the testing media and specimen conditions and their interactions significantly affected the flexural properties of the thermoplastic denture base polymers investigated ($p<0.001$). Figure 2 shows the UFS and FM results for several thermoplastic resins under the various test environments and specimen conditions. The tested-in-Dry/Air and/or tested-in-Wet/Air UFS values were significantly higher than those measured in the Wet/Water (ISO) condition for all thermoplastic resins except JC ($p<0.05$). In addition, the FM values of most polymers (except ES) were significantly higher in Dry/Air than Wet/Water (ISO) and/or Wet/Air ($p<0.05$). However, there was no significant increase in the FM values between Wet/Water (ISO) and Wet/Air conditions, except for AS and UG.

The water sorption values (μg/mm$^3$) of various thermoplastic specimens were determined and are shown in Fig. 3. The thermoplastic acrylates (AS and AT) exhibited significantly higher ($p<0.05$) water sorption than the polyamides, followed by the polycarbonate and polyester. The polypropylene (UG) displayed the lowest water sorption ($p<0.05$).
Table 2  The Means and SDs of flexural mechanical properties

<table>
<thead>
<tr>
<th>Group</th>
<th>Composition</th>
<th>Proportional limit</th>
<th>Ultimate flexural strength (UFS)</th>
<th>Corrected UFS</th>
<th>Maximum flexural strain</th>
<th>Flexural modulus</th>
<th>Energy absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PL (MPa)</td>
<td>σf (MPa)</td>
<td>σfc (MPa)</td>
<td>εf (%)</td>
<td>E (MPa)</td>
<td>EA (kJ/m²)</td>
</tr>
<tr>
<td>FV</td>
<td>Polyamide</td>
<td>10.4 (0.3)a</td>
<td>26.9 (0.7)a</td>
<td>32.9 (0.9)a</td>
<td>8.6 (0.9)a</td>
<td>612 (17)a</td>
<td>8.86 (0.25)a</td>
</tr>
<tr>
<td>FR</td>
<td>Polyamide</td>
<td>11.6 (0.3)a</td>
<td>28.0 (0.9)ab</td>
<td>34.8 (0.9)ab</td>
<td>8.4 (0.1)a</td>
<td>612 (23)a</td>
<td>8.94 (0.27)a</td>
</tr>
<tr>
<td>VP</td>
<td>Polyamide</td>
<td>12.5 (0.2)a</td>
<td>30.7 (0.6)b</td>
<td>37.0 (0.7)b</td>
<td>8.2 (0.2)bc</td>
<td>694 (20)b</td>
<td>9.56 (0.27)bc</td>
</tr>
<tr>
<td>LF</td>
<td>Polyamide</td>
<td>31.6 (2.6)c</td>
<td>57.4 (1.1)f</td>
<td>64.3 (1.3)f</td>
<td>7.2 (0.2)c</td>
<td>1,341 (30)c</td>
<td>15.25 (0.62)c</td>
</tr>
<tr>
<td>RN</td>
<td>Polyamide</td>
<td>31.7 (1.6)c</td>
<td>60.0 (1.6)e</td>
<td>70.6 (2.1)c</td>
<td>7.8 (0.2)cd</td>
<td>1,381 (34)c</td>
<td>17.77 (0.76)d</td>
</tr>
<tr>
<td>ST</td>
<td>Polyamide</td>
<td>33.2 (1.7)d</td>
<td>60.6 (1.1)g</td>
<td>69.8 (1.5)f</td>
<td>7.3 (0.1)g</td>
<td>1,358 (29)f</td>
<td>16.39 (0.38)ef</td>
</tr>
<tr>
<td>AT</td>
<td>Polymethyl methacrylate</td>
<td>19.2 (0.3)b</td>
<td>41.6 (0.7)c</td>
<td>46.0 (0.7)c</td>
<td>6.0 (0.1)b</td>
<td>1,412 (9)c</td>
<td>9.74 (0.38)b</td>
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<tr>
<td>FA</td>
<td>Polymethyl methacrylate</td>
<td>20.9 (0.4)b</td>
<td>44.3 (1.4)cd</td>
<td>48.8 (1.7)c</td>
<td>5.7 (0.1)b</td>
<td>1,416 (27)c</td>
<td>9.58 (0.23)b</td>
</tr>
<tr>
<td>SR</td>
<td>Polymethyl methacrylate</td>
<td>21.2 (0.5)b</td>
<td>45.6 (1.3)cd</td>
<td>48.8 (1.4)c</td>
<td>7.7 (0.2)c</td>
<td>1,354 (36)c</td>
<td>14.15 (0.77)cd</td>
</tr>
<tr>
<td>AS</td>
<td>Polymethyl methacrylate</td>
<td>25.2 (1.4)e</td>
<td>53.3 (0.9)e</td>
<td>58.1 (1.1)j</td>
<td>5.4 (0.3)e</td>
<td>1,783 (70)j</td>
<td>10.72 (0.91)j</td>
</tr>
<tr>
<td>ES</td>
<td>Polyester</td>
<td>31.3 (1.9)d</td>
<td>58.4 (2.1)g</td>
<td>60.8 (2.3)h</td>
<td>6.1 (1.1)g</td>
<td>1,569 (56)h</td>
<td>13.05 (0.63)c</td>
</tr>
<tr>
<td>UG</td>
<td>Polypropylene</td>
<td>11.3 (0.3)a</td>
<td>26.5 (0.7)a</td>
<td>32.5 (1.0)a</td>
<td>7.6 (0.2)a</td>
<td>829 (18)b</td>
<td>8.51 (0.23)a</td>
</tr>
<tr>
<td>JC</td>
<td>Polycarbonate</td>
<td>40.0 (0.8)c</td>
<td>89.4 (1.0)b</td>
<td>100.8 (1.2)c</td>
<td>6.7 (0.1)c</td>
<td>2,245 (48)bc</td>
<td>21.96 (0.58)b</td>
</tr>
</tbody>
</table>

Values with the same lower-case letters are not significantly different for each property (p<0.05; Sheffe’s multiple contrast test).

Table 3  Results of two-way ANOVA

<table>
<thead>
<tr>
<th>Source</th>
<th>Property</th>
<th>df</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material (A)</td>
<td>UFS</td>
<td>7</td>
<td>23.871</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>FM</td>
<td>7</td>
<td>26.681</td>
<td>0.000</td>
</tr>
<tr>
<td>Test condition (B)</td>
<td>UFS</td>
<td>2</td>
<td>11.563</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>FM</td>
<td>2</td>
<td>11.057</td>
<td>0.001</td>
</tr>
<tr>
<td>A * B</td>
<td>UFS</td>
<td>14</td>
<td>85.277</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>FM</td>
<td>14</td>
<td>88.817</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Fig. 2  Results of UFS (A) and FM (B) of thermoplastic denture base polymers in terms of test environment and storage condition. Horizontal lines indicate statistical insignificance in each material at p<0.05 level. Dotted lines indicate the minimum requirement of ISO 20795-1.

Fig. 3  Water sorption (Wsp) of thermoplastic polymer specimens. Horizontal lines indicate statistical insignificance in each material at p<0.05 level.
DICUSSION

This study demonstrated a wide variety of flexural mechanical behaviors of thermoplastic denture base polymers. The flexure testing of the machined specimen strips was well controlled in this study, and the results showed small coefficient of variation in the flexural mechanical properties (Table 2). Polyamide denture base resins can be categorized into two groups based on the flexural properties: 'soft-type' polyamide (e.g., FR, FV, and VP) and 'hard-type' polyamide (e.g., LF, RN, and ST). The flexural properties of hard-type polyamides were significantly higher than those of thermoplastic acrylate polymers and were similar to those of polyester resin (e.g., EstheShot Brite). The recently introduced thermoplastic denture base polymer polypropylene resin (Unigum) demonstrated a flexural strength similar to that of soft-type polyamides with a slightly higher FM. The polycarbonate (Jet Carbo-S) demonstrated outstanding flexural strength without breakage and was stronger than the conventional heat-polymerization acrylic resins (64–78 MPa) tested in the same conditions.

Since polymeric materials start to deform at low stresses during the flexural testing, the flexible property can be characterized by relative ratio of the PL to the UFS values (PL/UFS). The mean PL/UFS ratios of the thermoplastic resins (0.39–0.55) investigated were generally lower than those for the conventional heat-polymerizing acrylic resins (0.55–0.67) reported in previous study, indicating the high flexibility of thermoplastic denture base polymers. The soft-type polyamides and polypropylene materials show the lowest PL/UFS ratio (~0.4) with low flexural moduli. The behavior of these denture base polymers increase their comfort for denture-wearing patients and provides a soft fit. However, it has been demonstrated that denture base resins with a lower elastic modulus transmit a higher load to mucosa under the denture base and can irritate gum tissues and accelerate abnormal resorption of the residual alveolar ridge. Thus, a thermoplastic resin denture base designed with a metal framework has been recommended to address these issues.

The UFS and FM of all thermoplastic denture base resins investigated, except for JC, failed to fulfill the minimum requirements of ISO 20795-1 Type 3, which requires 65 MPa (UFS) and 2,000 MPa (FM). According to ASTM D790, the support span-to-depth ratio for flexural testing of polymer specimens should be 16 with a tolerance of ±1. If the span-to-depth ratio is greater than 16 and specimen deflects by more than 10% of the support span, the flexure strength can be corrected by Eq. 4. Although the span-to-depth ratio of the present test configuration was about 15.2, the maximum amounts of flexural deflection of specimens, ranged from approximately 7 mm (AS) to 11 mm (FV), were exceeded 10% of the support span length (50 mm). Therefore, the UFS of all the thermoplastic resins can be reasonably adjusted by the recommendation of ASTM D790. However, even though this correction is considered in determining the UFS (Corrected UFS in Table 2), only two materials (RN and ST) fulfilled the ISO 20795-1 requirement. These results suggest a revision should be considered for the flexural property requirements of ISO 20795-1 Type 3 (thermoplastic resin). The polycarbonate (JC) exhibited 89 MPa UFS and 2,245 MPa FM and is the only thermoplastic denture polymer meeting the ISO requirement for flexural properties.

The null hypothesis of this study, that the test environment and specimen conditions do not affect the flexural properties of thermoplastic resins, was rejected because the test variations severely influenced the UFS and FM (Fig. 2). We found that drying the thermoplastic specimens (Dry/Air group) in a desiccator significantly increased the UFS and FM relative to the values in the corresponding Wet/Water group. The results were more prominent for the polyamides (FV and VP) and thermoplastic acrylates (AT and AS). The FM value was generally less sensitive to the effect of the test environment. The polypropylene material (UG) with the least water sorption (0.26 μg/mm²) exhibited increases in UFS and FM values approximately 30% when tested in ambient air. These findings support an earlier report demonstrating that the flexural load of acrylic denture resins decreases when tested in 37°C water compared to air. This behavior of the denture base polymers may be explained by the role of water molecules at the strained surface of specimens during the flexure test. Our data indicate that water immersion significantly decreases the flexural mechanical properties of some thermoplastic denture base polymers. Therefore, to choose thermoplastic resin products with desirable flexible mechanical properties, comparison of tested values from water immersion conditions according to ISO 20795-1 is recommended.

CONCLUSIONS

The UFS and FM of thermoplastic denture base polymers investigated in this study did not meet the requirements of ISO 20795-1, except for polycarbonate material. Therefore, revising the required flexural mechanical properties for thermoplastic denture resin is strongly recommended. Significant effects of test medium (water) and specimen conditions on the flexural mechanical
properties were found. Water immersion during testing significantly decreased the flexural strength and modulus of several polyamides by approximately 50% relative to the values in the dried test conditions. Therefore, when measuring or comparing the flexural mechanical properties of denture base polymers, it is important to indicate the test media and specimen conditions.

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