Characteristics of low polymerization shrinkage flowable resin composites in newly-developed cavity base materials for bulk filling technique

Keiko NITTA¹, Rie NOMOTO¹, Yuji TSUBOTA¹², Masuji TSUCHIKAWA³⁴ and Tohru HAYAKAWA¹

¹ Department of Dental Engineering, Tsurumi University School of Dental Medicine, 2-1-3 Tsurumi, Tsurumi-ku, Yokohama, Kanagawa 230-8501, Japan
² Tsubota Dental Clinic, 4-7-14 Kohinata, Bunkyo-ku, Tokyo 112-0006, Japan
³ Department of Removable Prosthodontics, Tsurumi University School of Dental Medicine, 2-1-3 Tsurumi, Tsurumi-ku, Yokohama, Kanagawa 230-8501, Japan
⁴ Sun Medical, 571-2 Furutaka-cho, Moriyama, Shiga 524-0044, Japan
Corresponding author, Keiko NITTA; E-mail: uchida-k@tsurumi-u.ac.jp

The purpose of this study was to evaluate polymerization shrinkage and other physical properties of newly-developed cavity base materials for bulk filling technique, with the brand name BULK BASE (BBS). Polymerization shrinkage was measured according to ISO/FDIS 17304. BBS showed the significantly lowest polymerization shrinkage and significantly higher depth of cure than conventional flowable resin composites (p<0.05). The Knoop hardness, flexural strength and elastic modulus of that were significantly lower than conventional flowable resin composites (p<0.05). BBS had the significantly greatest filler content (p<0.05). SEM images of the surface showed failure of fillers. The lowest polymerization shrinkage was due to the incorporation of a new type of low shrinkage monomer, which has urethane moieties. There were no clear correlations between inorganic filler contents and polymerization shrinkage, flexural strength and elastic modulus. In conclusion, the low polymerization shrinkage of BBS will be useful for cavity treatment in dental clinics.

Keywords: Polymerization shrinkage, Low polymerization shrinkage monomer, Flowable resin, Bulk fill resin, Archimedes’ principle

INTRODUCTION

Flowable resin composites have some advantages such as better adaptation to the tooth surface, easier and swifter handling properties during restoration, higher flexibility, etc., due to their low viscosity¹². Flowable resin composites are widely used, for example, in preventive resin restorations for minimally invasive occlusal Class I type, minimal invasive Class II restorations, restorations of Class V abfraction lesions and cavity liner for improving the initial marginal integrity.¹³ Moreover, some flowable composite resins have been marketed as cavity base materials for bulk filling technique.⁶⁻⁸ Cavity base flowable composite resins for bulk filling technique can fill the most part of the cavity in one bulk, and can reduce clinical steps and treatment time compared with conventional incremental filling. However, polymerization shrinkage is a serious problem for flowable resin composites. Flowable resin composites generally show higher polymerization shrinkage than conventional restorative resin composites. The increase of filler content in flowable resin composite is limited in order to maintain its flowability. This decrease of inorganic filler content corresponds with an increase of monomer content, leading to the increase of polymerization shrinkage.⁹ The occurrence of polymerization shrinkage in a restoration can lead to secondary caries, pulpal damage, and debonding of restorative appliances due to gap formation between restorative materials and cavity walls.

Some approaches have been reported for reducing polymerization shrinkage by developing new monomers. Ring-opening polymerization of epoxy compounds is known to cause lower shrinkage than free-radical vinyl polymerization. Stansbury introduced novel monomers with spiro-ortho compounds and insisted that the ring-opening polymerization of spiro-orthocarbonate groups drastically reduced the polymerization shrinkage.¹⁰ Some spiro-ortho monomers have been reported for reducing polymerization shrinkage.¹¹⁻¹³ Weinmann et al.¹⁴ developed a new monomer system, silolane, obtained from the reaction of oxirane and siloxane molecules. The ring-opening polymerization of oxirane moieties in silolane molecule caused low polymerization shrinkage. Stefanosilane-based monomers are now used as a component of commercially available resin composites.⁴⁻¹⁵⁻¹⁷ Recently, low polymerization shrinkage (LPS) dimethacrylate monomers with urethane moieties have been developed and commercially available as a component of cavity base materials, with the brand name “BULK BASE” (BBS). BBS has almost the same flowability as conventional flowable resin composites. It is expected that low polymerization cavity base materials will cause less damages to tooth substance including dental pulp and fewer and smaller contraction gaps due to less stress during the polymerization process. The purpose of this study was to evaluate the polymerization shrinkage, depth of cure, Knoop hardness, flexural strength and inorganic filler content of BBS by comparing other commercially available cavity base composites and conventional flowable composites. In particular, the polymerization shrinkage...
was measured according to ISO/FDIS 17304, which is based on Archimedes’ principle.

MATERIALS AND METHODS

Materials
The five flowable resin composites used in this study are shown in Table 1. Monomers and fillers are also listed in Table 1. BBM (BULK BASE Medium flow), BBH (BULK BASE High flow) and FBF (Filtek Bulk Fill) are classified as cavity base materials and FSU (Filtek Supreme Ultra) and MI (MI flow) are conventional flowable composites. Structural formulae of LPS monomer is listed in Fig. 1. For light curing, an LED light curing unit with a tip diameter of 10 mm (1,200 mW/cm², Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein) was used.

Polymerization shrinkage
Polymerization shrinkage of the five flowable resin composites was investigated according to ISO/FDIS 17304. The density determination apparatus is shown in Fig. 2. This apparatus consists essentially of a platform, beaker, pan hanger assembly, and thermometer. Sodium lauryl sulphate aqueous solution (1 wt%) was used as the buoyancy medium in this study. The densities of the unpolymerized and polymerized flowable resin composite were determined by Archimedes’ principle.

Individual density of each unpolymerized flowable resin composite, \( \rho_u \), and that of each polymerized flowable resin composite, \( \rho_c \), were obtained by measurement of the weight of each in air and in buoyancy medium. Afterwards, the polymerization shrinkage, \( S \), was determined using formula (1).

\[
S = \left( \frac{\rho_c - \rho_u}{\rho_c} \right) \times 100
\]

\( \rho_u \) (g/mL) is the density of the unpolymerized specimen, and \( \rho_c \) (g/mL) is the density of the polymerized specimen.

Table 1 Flowable resin composites used in this study

<table>
<thead>
<tr>
<th>Materials</th>
<th>Manufacture</th>
<th>Color</th>
<th>Composition</th>
<th>Filler</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>BULK BASE Medium flow</td>
<td>Sun Medical</td>
<td>—</td>
<td>Bis-MPEPP Acrylic monomers</td>
<td>Barium-silica-glass</td>
<td>BBM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fluoloaluminosilicate-glass</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1, 3, 5 μm)</td>
<td></td>
</tr>
<tr>
<td>BULK BASE High flow</td>
<td>Sun Medical</td>
<td>—</td>
<td>Bis-MPEPP Acrylic monomers</td>
<td>Barium-silica-glass</td>
<td>BBH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fluoloaluminosilicate-glass</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1, 3, 5 μm)</td>
<td></td>
</tr>
<tr>
<td>Filtek Bulk Fill</td>
<td>3M ESPE</td>
<td>U</td>
<td>Bis-GMA UDMA Bis-EMA</td>
<td>Zirconia/silica</td>
<td>FBF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Procrylat resins</td>
<td>ytterbium trifluoride filler</td>
<td></td>
</tr>
<tr>
<td>Filtek Supreme Ultra</td>
<td>3M ESPE</td>
<td>A2</td>
<td>Bis-GMA TEGDMA Procrylat resins</td>
<td>ytterbium trifluoride filler</td>
<td>FSU</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.1–5 μm)</td>
<td></td>
</tr>
<tr>
<td>MI flow</td>
<td>GC</td>
<td>A2</td>
<td>Bis-MEPP</td>
<td>Strontium glass</td>
<td>MI</td>
</tr>
</tbody>
</table>
**Depth of cure**
Five specimens of each flowable resin composite were prepared. A stainless steel cylindrical split-mold of height 10 mm and internal diameter 4 mm was used. The mold was overfilled with each flowable resin composite and polyester strips (Matrix Tape, 3M ESPE, St. Paul, MN, USA) were placed on top of the material. Each specimen was irradiated for 20 s using a LED cure unit. The curing light guide tip was kept centered and in contact with the mold.

At 3 min after the photo irradiation, the specimen was removed from the mold and the bottom surface was scraped to remove the soft unpolymerized resin using a plastic spatula. The maximum thickness of cured material was measured with a micrometer.

**Knoop hardness**
After the measurement of the depth of cure, each specimen was sectioned perpendicularly to the irradiated surface using a cutting machine under running water. The sectioned surface was polished using 4000-grid silicon carbide paper under continuous irrigation by distilled water. Knoop hardness was measured at 0.5 and 3.0 mm from the irradiated surface using a micro hardness tester (HMV-1, Shimadzu, Kyoto, Japan) with a 980.7 mN load and a dwell time of 30 s.

**Flexural strength and elastic modulus**
Five specimens (2×2×25 mm) of each material were prepared using a stainless mold. Each flowable resin composite was filled in the mold and covered with a polyester strip. Each specimen was polymerized using the LED curing unit. All specimens were then stored in distilled water at 37°C prior to testing for 24 h.

Three-point bending tests, with a support span length of 20 mm, were performed using a universal testing machine (AG-IS 20kN, Shimadzu) at a cross-head speed of 0.75 mm/min. The flexural strength and elastic modulus were obtained by fracture load, deflection and elastic limit according to the three-point bending formula.

**Inorganic filler contents**
Inorganic filler contents were obtained according to ISO4049:1978(20). First, a ceramic crucible was heated in a furnace (AUTO FURNACE, GC, Tokyo, Japan) at 575±25°C and then cooled in a desiccator. The constant weight of the crucible (m₁) was obtained. After placing 300 mg of flowable resin composite paste in the crucible the whole weight (m₂) was determined. The resin paste was heated in the crucible, and the whole weight after heating and cooling (m₃) was determined until the constant weight was within 0.001 g by repeating the cycle of heating and cooling. The filler content is given by formula (2) as a percentage.

\[
\text{Filler content} = \left( \frac{m₂ - m₁}{m₃ - m₁} \right) \times 100
\]

Three runs were performed and mean values were obtained.

**Statistical analysis**
Data were analyzed using one-way analysis of variance (ANOVA) and Fisher’s test with Minitab 12.22 (Minitab, State College, PA, USA). The non-paired t-test was used to compare data from Knoop hardnesses at 0.5 mm and at 3.0 mm for each flowable resin composite. p Values of less than 0.05 were considered significant and data were expressed as the mean±standard deviation (SD).

**RESULTS**
The results of the polymerization shrinkage are shown in Fig. 3. Average polymerization shrinkage values ranged from 2.14% (BBM) to 3.73% (MI). Significant differences were seen in the polymerization shrinkage among five flowable resin composites (p<0.05). BBM showed significantly the lowest and MI showed the highest polymerization shrinkage (p<0.05).

Table 2 lists the depth of cure, Knoop hardness, flexural strength, elastic modulus and filler contents of each flowable resin composite. For depth of cure, FBF showed significantly the greatest value among the tested materials (p<0.05). For Knoop hardness, BBM showed significantly the greatest value among the tested materials (p<0.05). There were no significant differences in depth of cure between BBM and BBH (p>0.05), or between FSU and MI (p>0.05).

Comparing Knoop hardness at 0.5 mm from the irradiated top surface, the Knoop hardness of BBM...
Table 2  Mean and standard deviations for depth of cure (mm), Knoop hardness (KHN), flexural strength (MPa), elastic modulus (GPa) and filler content (wt%)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Depth of cure (mm)</th>
<th>KHN 0.5 mm</th>
<th>KHN 3.0 mm</th>
<th>Flexural strength (MPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Filler content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBM</td>
<td>7.9 (0.1)a</td>
<td>36.3 (2.7)a</td>
<td>26.4 (3.8)c</td>
<td>96.2 (4.4)a</td>
<td>5.8 (0.2)</td>
<td>70.5 (0.2)</td>
</tr>
<tr>
<td>BBH</td>
<td>7.9 (0.1)a</td>
<td>31.1 (4.5)b</td>
<td>24.7 (2.3)d</td>
<td>89.0 (4.3)a</td>
<td>5.1 (0.3)</td>
<td>68.7 (0.4)</td>
</tr>
<tr>
<td>FBF</td>
<td>9.9 (0.2)</td>
<td>32.0 (2.3)b</td>
<td>31.5 (2.5)b</td>
<td>132.8 (7.7)hc</td>
<td>6.7 (0.3)</td>
<td>60.9 (0.1)</td>
</tr>
<tr>
<td>FSU</td>
<td>5.6 (0.0)b</td>
<td>40.2 (2.9)c</td>
<td>34.6 (1.3)b</td>
<td>126.8 (10.6)b</td>
<td>7.6 (0.3)a</td>
<td>58.8 (0.1)</td>
</tr>
<tr>
<td>MI</td>
<td>5.6 (0.1)a</td>
<td>41.5 (1.9)c</td>
<td>27.8 (3.1)c</td>
<td>138.8 (9.0)c</td>
<td>7.9 (0.4)a</td>
<td>64.8 (0.4)</td>
</tr>
</tbody>
</table>

Same letters are not significantly different (p>0.05).

Fig. 4  SEM micrograph of investigated materials.

Fig. 5  Relationship between the inorganic filler content and the polymerization shrinkage (a), the flexural strength (b) and the elastic modulus (c).
was significantly higher than those of BBH and FBF ($p<0.05$), and significantly lower than that of MI ($p<0.05$). There were no significant differences in Knoop hardness at 3.0 mm between BBM and BBH ($p>0.05$) or between FBF and FSU ($p<0.05$). The Knoop hardnesses of BBM and BBH were significantly lower than those of FBF and FSU ($p<0.05$).

Flexural strengths of BBM and BBH were significantly lower than those of FBF, FSU and MI ($p<0.05$). There were no significant differences in flexural strength between BBM and BBH ($p>0.05$), between FBF and FSU ($p>0.05$) and between FBF and MI ($p>0.05$).

Regarding elastic modulus, BBM, BBH and FBF showed significantly lower elastic moduli than FSU and MI ($p<0.05$). No significant difference was found between FSU and MI ($p>0.05$).

Inorganic filler content ranged from 58.8 to 70.5 wt%. Statistically significant differences were observed among the five flowable resin composites. BBM had significantly the greatest filler content ($p<0.05$) and FSU had the lowest ($p<0.05$).

SEM images of the polished surface of each flowable resin composite are shown in Fig. 4. Larger and irregular shapes of fillers could be observed for BBM and BBH. Failure of fillers during the polishing was recognized. Agglomeration of filler particles was observed in FBF, FSU and MI.

Further, the relationships between the inorganic filler content and the polymerization shrinkage, flexural strength, elastic modulus were analyzed. As shown in Fig. 5a, there was no clear correlation between inorganic filler content and polymerization shrinkage. Flexural strength and elastic modulus also showed no clear correlation with filler contents as shown in Figs. 5b and c.

**DISCUSSION**

In the present study, the polymerization shrinkage, depth of cure, Knoop hardness, flexural strength and inorganic filler content of a newly-developed cavity base material, BBS, were established by comparing other commercially available bulk base composites and conventional flowable composites.

As mentioned above, some flowable composite resins are now used for cavity base materials for bulk filling technique\(^6\)\(^-\)\(^8\). BBS is now commercially available as a bulk base composite resin for bulk filling technique in Japan and contains a new type of low polymerization shrinkage monomer, namely LPS monomer.

Various methods have been reported for evaluating polymerization shrinkage of resin composites, such as mercury dilatometer\(^6\)\(^,\)\(^21\), bonded disk method\(^22\)\(^,\)\(^23\), optical method\(^24\)\(^,\)\(^25\), use of the strain gauge\(^26\), linear shrinkage\(^27\)\(^,\)\(^29\) \textit{etc}. Monteiro \textit{et al.} compared the polymerization shrinkage of resin composites using three different methods; coordinate measuring machine (CMM), optical coherence tomography (OCT) and Archimedes’ principle\(^30\). They claimed that the different methods for measuring polymerization shrinkage provided significantly different values of polymerization shrinkage. In the present study, we employed the methods recommended by ISO\(^30\). The method based on Archimedes’ principle is the only method for measuring polymerization shrinkage recommended by ISO.

The method based on Archimedes’ principles has advantages of convenience and accuracy compared with the other methods mentioned above, and can capture the entire volumetric change\(^30\). This method is also reasonably insensitive to temperature changes\(^31\). Aqueous solution of sodium lauryl sulfate, a surface-active agent, was used as the buoyancy medium in this study. The adherence of air bubbles to the samples, which can cause incorrect measurements, was avoided by using sodium lauryl sulfate\(^25\)\(^,\)\(^30\)\(^,\)\(^31\).

It revealed that the polymerization shrinkage of BBS was effectively reduced. This was due to the presence of LPS monomer in BBS. The LPS monomer in BBS has a dimethacrylate structure with urethane moieties. LPS monomer has steric bulky groups in its structure\(^18\). Steric bulky groups cause low polymerization shrinkage but decrease the mechanical properties of cured resin. The urethane structure inhibited this decrease of the mechanical properties.

Moreover, BBS includes Bis-MPEPP and acrylate ester monomer in addition to LPS monomer. Masudi \textit{et al.} reported that a significantly small value of polymerization shrinkage was obtained from the polyfunctional monomers diluted with Bis-MPEPP (2, 2-bis [4-(2 methacryloxyethoxyphenyl] propane)\(^22\). The low polymerization shrinkage in BBM and BBH is attributed to the combination of LPS and Bis-MPEPP. Low polymerization shrinkage will be advantageous for bulk base materials, preventing gap formation between the composite resin and cavity wall.

In contrast, the flexural strength and elastic modulus of BBS were inferior. Poor mechanical properties are a disadvantage for cavity base materials. SEM observation indicated the failure of fillers in BBS after polishing. This was due to insufficient bonding of the fillers to the resin matrix by unsatisfactory silane coupling agent treatment. The insufficient bonding of fillers might be one of the reasons for inferior mechanical properties of BBS. Improvement of these mechanical properties is necessary, although such filler failures do not occur in the clinical situation because cavity base materials need no polishing.

Generally, filler content correlates linearly with polymerization shrinkage, \textit{i.e.}, a greater amount of filler content corresponds with less polymerization shrinkage. However, in the present study, no linear correlation was identified between filler content and polymerization shrinkage. The flexural strengths and elastic modulus also showed no linear correlation with filler contents. Park \textit{et al.} evaluated the polymerization shrinkage, flexural and compressive properties of low-shrinkage composite resin\(^17\). They found that filler contents lineally correlated with polymerization shrinkage, but not with flexural strength. They speculated that the low correlation of flexural strength with filler content
is probably due to the fact the flexural strength being related more to the volume of material and internal defects such as cracks or voids that are generated during the manufacturing process. In the present study, the bonding between filler and monomer was insufficient in BBS as mentioned above. This may be one of the reasons for non-linear correlation between filler content and flexural strength or elastic modulus. The reason for non-linear correlation between filler content and polymerization shrinkage is not clear. Ku et al. reported that polymerization shrinkage was less correlated with filler content for commercially available flowable resins. It is well known that the degree of photo polymerization of photo-curable composite resins depends on the differences of refractive indexes, kinds of monomers or fillers, shape and distribution of fillers and photo polymerization initiators, etc., besides filler content. More detailed studies such as monomer contents including LPS monomers and/or filler shape and distribution are needed.

The filler size or filler distribution will influence the surface roughness or smoothness of resin composite. BBS showed larger size and more irregular shapes of fillers, which might cause aesthetic problems. However, BBS is used as a cavity base and thus there is no need for smooth surface.

Polymerization or adhesiveness of resin composites is affected by the light intensity of light curing unit. A cavity base material is applied on the cavity wall and floor, and thus the light guide tip cannot be placed close to the restored resin composite. Light intensity decreased with increasing distance between the light guide tip and the surface of resin composites. The decreased light intensity can be compensated for extending the irradiation time. In the clinical situation, it is important to use a longer irradiation time for the polymerization of cavity base materials.

Silorane-based resin composites are known to exhibit low polymerization shrinkage. However, Silorane-based resin composites are a conventional filling resin composite and cannot be used as a flowable resin composite. In contrast, BBS has low polymerization shrinkage with appropriate flowability. The cavity base technique will be widely applied in dental clinics. Adhesiveness of cavity base composite resin to the dentin cavity is an important factor for safe use. The bond strength of BBS to dentin will be studied in our next series of experiments.

In conclusion, it can be elucidated that the newly-developed cavity base material, BBS, has a low degree of polymerization shrinkage offering an advantage as a cavity base material and will be useful for cavity treatment in dental clinics.

REFERENCES

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