Regional ultimate tensile strength and water sorption/solubility of bulk-fill and conventional resin composites: The effect of long-term water storage

Ghassan RUMMANI¹, Kurumi IDE¹, Keiichi HOSAKA², Antonin TICHY¹,³, Ahmed ABDOU¹,⁴, Masayuki OTSUKI¹ and Masatoshi NAKAJIMA¹

¹ Department of Cariology and Operative Dentistry, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University, 1-5-45 Yushima, Bunkyo-ku, Tokyo 113-8510, Japan
² Department of Regenerative Dental Medicine, Tokushima University Graduate School of Biomedical Sciences, 3-18-15 Kuramoto-cho, Tokushima 770-8504, Japan
³ Institute of Dental Medicine, First Faculty of Medicine of the Charles University and General University Hospital in Prague, Karlovo namesti 32, Prague 121 11, Czech Republic
⁴ Biomaterials Department, Faculty of Dentistry, Modern University for Technology and Information, El-hadaba El-Wosta, Mokatam, 5th district, Cairo 11571, Egypt

Corresponding author, Masatoshi NAKAJIMA; E-mail: nakajima.ope@tmd.ac.jp

The effect of long-term water storage on the regional ultimate tensile strength (UTS), water sorption (Wₚ) and water solubility (Wₛ) of conventional and bulk-fill resin composites at various depths was investigated. Composite specimens light-cured from one side were sectioned into beams corresponding to different depths (1–5 mm) and stored in water for 24 h, 1 week, 1 month, 6 months or 1 year. UTS increased during the first week and then gradually decreased over time, especially in deeper regions. Bulk-fill composites initially exhibited similar UTS at all depths, whereas the UTS of conventional composites at 1 mm and 5 mm differed significantly at all time points. Wₚ and Wₛ increased with depth and storage time, markedly at 3–5 mm after 1 month for conventional composites and after 6 months for bulk-fill composites. The signs of degradation at depths beyond 3 mm suggested that even bulk-fill composites have suboptimal properties in layers more than 3 mm in thickness.

Keywords: Resin composite, Bulk-fill, Polymerization, Mechanical properties, Degradation

INTRODUCTION

Light-cured resin-based composites (RBCs) have become the most widely used direct restorative materials¹. However, they require incremental placement to reduce the polymerization shrinkage stress and to ensure adequate polymerization²,³. The polymerization behavior of light-cured RBCs is dependent upon several factors, e.g. radiant exposure, irradiance, the type and content of monomers and fillers, the concentration of photoinitiators, or the optical properties of the RBC⁴. Given the attenuation of light passing through RBCs, conventional RBCs cannot be sufficiently polymerized at depths greater than 2 mm. On the other hand, bulk-fill RBCs which have been recently introduced to the dental market are claimed to be adequately cured up to the thicknesses of 4–5 mm, which is achieved by their higher translucency compared to conventional RBCs³,⁵.

The depth of cure of light-cured RBCs has been most commonly investigated using the simple scraping method described by ISO 4049⁶. More complex methods evaluate the quality of polymerization at various depths, either directly by measuring the degree of conversion using infrared spectroscopy³,⁷ or indirectly by characterizing the mechanical properties of the RBCs³,⁸. Among them, microhardness has been often measured because the testing is simple and the values are correlated with the degree of conversion⁹. However, microhardness is strongly affected by filler load, type and particle size; therefore, it cannot be used for comparisons of polymerization quality between various RBCs. In contrast, the microtensile strength testing of the regional ultimate tensile strength (UTS) of RBCs was reported to be a suitable method for the evaluation of curing depth and for comparisons between different RBCs¹¹.

It is also well known that the mechanical properties of RBCs, such as strength and the modulus of elasticity, are influenced by water uptake. When RBCs are immersed in water, the resin matrix rapidly absorbs water, and its mechanical properties decrease compared to dry conditions¹²,¹³. This is caused by the swelling, plasticization¹⁴, and weakening of the three-dimensional polymer network¹⁵. Additionally, long-term immersion in water may result in the hydrolytic degradation of the matrix¹⁶, thus increasing the solubility and net water uptake of RBCs and further reducing their mechanical properties¹⁷. This effect may be even more pronounced in deeper layers of light-cured RBCs where the quality of polymerization is lower due to the decreased light energy¹⁷,¹⁸. Even though RBCs may initially seem to be adequately polymerized, long-term immersion in water might deteriorate their mechanical properties in deeper regions more markedly than near the surface, because the degree of conversion is gradually decreasing with depth¹¹,¹⁹,²⁰.
However, the effect of long-term water immersion on the regional UTS of light-cured RBCs at the different depths has not been sufficiently examined. Therefore, this study aimed to assess the regional UTS of bulk-fill and conventional RBCs in dry conditions and after various periods of water storage. In addition, the regional water sorption ($W_{sp}$) and solubility ($W_{sl}$) of the RBCs was evaluated. The null hypothesis was that the storage conditions would not significantly affect the regional UTS and $W_{sp}/W_{sl}$ of the tested bulk-fill and conventional RBCs.

**MATERIALS AND METHODS**

Three bulk-fill RBCs —Beautifil Bulk (BFB; Shofu, Kyoto, Japan), Filtek Bulk Fill (FTB; 3M ESPE, St. Paul, MN, USA), and Tetric EvoCeram Bulk Fill (TEC; Ivoclar Vivadent, Schaan, Liechtenstein)— and three conventional RBCs —Beautifil II (BFII; Shofu), Clearfil Majesty ES2 (CES2; Kuraray Noritake Dental, Tokyo, Japan), and MI Gracefil (MIGF; GC, Tokyo, Japan) were used in this study (Table 1). To standardize light penetration through the RBCs, A2 or universal shades were selected.

**Specimen preparation**

A cylindrical cavity (5 mm in depth, 8 mm in diameter) was prepared in a cubic ABS resin block (1 cm³), and its impression was taken (Exahiflex, GC) to fabricate replicas from a dual-cured RBC (Estecore, Tokuyama Dental, Tokyo, Japan). The replicas were light-cured for 60 s using a QTH light-curing unit (Optilux 500, Demetron/Kerr, Danbury, CT, USA), followed by 10 min using a laboratory light-curing unit (α-light II, J. Morita, Tokyo, Japan) to ensure maximal polymerization. The replicas were stored in distilled water at 37°C for 1 week. Then, all external surfaces of the replicas were covered with a black vinyl tape to prevent the penetration of light through the walls during light-irradiation, except for the surface with the orifice of the cavity. The cavities were filled with one of the RBCs in a single increment, a plastic strip was placed over the top surface, and excess material was pushed out with a glass slide. The specimens were light-cured for 20 s by placing the tip of the light curing unit (Optilux 500, Demetron/Kerr) on the top of the cavity. The radiant exitance of the light-curing unit (620 mW/cm²) was measured using an integrating sphere.

After the specimens were stored for 24 h in dry and dark conditions at room temperature (23°C), the composite specimens of each material ($n$=60) were randomly divided into six experimental groups ($n$=10) according to the storage conditions: immediate testing (control group) and storage in distilled water at 37°C.

![Table 1: Resin composite materials used in this study](image-url)
for 24 h, 1 week, 1 month, 6 months or 1 year. The immediate testing and 24-h storage were conducted to assess the development of mechanical properties shortly after polymerization. As the properties of RBCs should stable after 1 week, the 1-week data were considered a baseline for comparisons with the longer storage periods representing short-, medium- and long-term aging. Each specimen was sectioned parallel to axial walls using a low-speed diamond saw (Isomet, Buehler, Lake Bluff, IL, USA) to obtain two slabs 2 mm in width from the central region. One of the slabs was used for the measurements of UTS while the other slab was used for the measurement of $W_{sp}$ and $W_{sl}$. The slabs were serially sectioned parallel to the surface of the cavity in 1 mm intervals, and given the 0.3 mm thickness of the blade, five beams 0.7 mm in thickness representing different depth levels were obtained (Fig. 1).

**Measurement of regional ultimate microtensile strength**

After the designated storage periods, beams for the measuring of UTS were trimmed to an hour-glass shape (0.7 mm width in the narrowest region) using a fine diamond bur in a high-speed handpiece. A digital caliper (Mitutoyo, Tokyo, Japan) was used to measure the cross-sectional area of each beam. Prior to testing, each beam was also inspected using a stereomicroscope for cracks and other flaws. The non-trimmed ends of the beams were glued to a microtensile testing jig using a cyanoacrylate glue (Zapit, DVA, Anaheim, CA, USA) and stressed in tension in a table-top testing machine (EZ Test, Shimadzu, Kyoto, Japan) at a crosshead speed of 1 mm/min. The UTS was calculated by dividing the force at failure by the cross-sectional area of the beam.

**Measurement of regional water sorption and solubility**

The dimensions of beams intended for the measurement of $W_{sp}$ and $W_{sl}$ were measured using the digital caliper and their volume ($V$) was calculated. The beams were stored in a light-proof desiccator with a self-indicating silica gel at 37°C and weighed on an analytical balance daily until a stable initial mass ($m_i$) was obtained. The beams were then immersed in distilled water, stored at 37°C, and after the designated storage periods of 24 h, 1 week, 1 month, 6 months, or 1 year, they were gently dried with an absorbent paper and weighed to obtain the mass in wet state ($m_2$). Subsequently, the beams were placed in a desiccator and weighed daily until their mass stabilized ($m_3$). $W_{sp}$ and $W_{sl}$ were calculated using the following formulas and expressed in μg/mm³:

\[
W_{sp} = \frac{(m_2 - m_3)}{V} \quad (Eq. 1),
\]

\[
W_{sl} = \frac{(m_1 - m_3)}{V} \quad (Eq. 2).
\]

**Statistical analysis**

The UTS, $W_{sp}$, and $W_{sl}$ data showed non-normal distributions when assessed using the Kolmogorov-Smirnov and Shapiro-Wilk tests. For each RBC, comparisons between values at different thickness and storage conditions were performed using the Kruskal-Wallis test followed by multiple comparisons of all pairs with the Steel-Dwass method. The significance level was set at $\alpha=0.05$ (JMP 13.2.1, SAS Institute, Cary, NC, USA).

**RESULTS**

**UTS**

Mean UTS values and standard deviations of each RBC at different depth levels are presented in Table 2. Compared to the control group, the UTS of all tested materials increased over the first week of water storage, but the increase was significant only for TEC at the depth of 2 mm and 4 mm ($p<0.05$). Further water storage gradually decreased the UTS of all RBCs. Compared to the 1-week values, a significant decrease ($p<0.05$) was observed for BFII at depths ≥4 mm after 1 month, for FTB at 5 mm after 1 month and at ≥3 mm after 6 months, for TEC at ≥4 mm after 1 month, at ≥2 mm after 6 months and at all depths after 1 year, for CES2 at 3–4 mm after 6 months and at all depths after 1 year, and for MIGF at ≥2 mm after 6 months. For BFII, water storage
Table 2  Regional ultimate microtensile strength in MPa (mean±S.D.)

|        | 1 mm | 2 mm | 3 mm | 4 mm | 5 mm |
|--------|------|------|------|------|------|
| BFB    |      |      |      |      |      |
| Dry    | 74.9±14.0 | 67.6±14.1 | 66.9±14.4 | 65.4±9.5 | 65.9±12.2 |
| 24 h   | 75.7±8.0   | 70.2±10.2 | 67.6±8.8   | 66.4±9.2 | 66.4±13.4 |
| 1 week | 76.1±13.6 | 72.7±12.0 | 71.8±10.0 | 68.9±11.8 | 66.7±11.3 |
| 1 month| 72.1±10.2 | 69.7±11.1 | 67.9±9.2   | 56.2±11.2 | 53.9±15.8 |
| 6 months| 70.8±14.2 | 69.4±10.1 | 65.5±13.2 | 45.5±8.0  | 42.8±7.8  |
| 1 year | 69.5±13.4 | 64.7±11.8 | 57.5±13.1 | 40.4±9.9  | 40.0±11.7 |
| FTB    |      |      |      |      |      |
| Dry    | 78.3±12.3 | 75.2±16.3 | 77.6±11.2 | 65.7±14.0 | 63.4±10.7 |
| 24 h   | 83.6±13.9 | 80.7±13.5 | 81.4±14.0 | 72.6±14.4 | 77.3±9.8  |
| 1 week | 84.8±9.4   | 81.9±13.2 | 81.0±13.6 | 72.3±12.8 | 77.1±14.7 |
| 1 month| 71.6±14.2 | 66.1±15.7 | 63.2±13.5 | 56.7±14.3 | 55.4±11.8 |
| 6 months| 69.7±12.3 | 61.9±13.9 | 57.7±11.9 | 49.6±9.0  | 46.2±9.7  |
| 1 year | 69.0±12.1 | 62.2±12.6 | 54.7±9.1  | 43.7±9.2  | 39.2±11.1 |
| TEC    |      |      |      |      |      |
| Dry    | 63.9±12.1 | 58.3±7.4  | 57.4±11.8 | 57.9±7.8  | 54.7±14.2 |
| 24 h   | 73.5±10.8 | 70.5±8.1  | 68.2±10.7 | 69.6±8.5  | 62.1±12.7 |
| 1 week | 77.6±11.5 | 76.0±9.1  | 74.5±9.0  | 73.0±8.6  | 71.1±11.0 |
| 1 month| 62.9±12.3 | 62.2±13.0 | 59.7±14.8 | 48.5±16.0 | 46.0±12.3 |
| 6 months| 59.8±6.9  | 54.6±6.9  | 51.1±9.9  | 38.4±11.6 | 34.1±6.3  |
| 1 year | 56.9±12.1 | 53.3±7.4  | 49.4±11.8 | 37.9±7.8  | 35.1±7.1  |
| BFII   |      |      |      |      |      |
| Dry    | 80.3±12.0 | 74.0±12.6 | 73.5±13.8 | 73.2±12.6 | 59.9±10.6 |
| 24 h   | 83.9±6.9   | 74.2±6.9  | 74.6±13.3 | 68.1±7.2  | 61.4±12.4 |
| 1 week | 84.3±11.1 | 74.6±12.6 | 74.0±9.1  | 70.1±10.4 | 61.0±9.8  |
| 1 month| 80.0±9.2   | 71.4±9.9  | 67.9±9.2  | 56.7±15.9 | 45.9±12.2 |
| 6 months| 79.8±10.4 | 70.9±8.6  | 67.8±11.4 | 56.6±11.8 | 45.0±12.6 |
| 1 year | 79.0±11.9 | 70.3±16.1 | 67.2±14.2 | 56.0±9.9  | 43.7±12.1 |
| CES2   |      |      |      |      |      |
| Dry    | 49.8±14.2 | 46.2±9.3  | 47.0±6.2  | 40.1±6.3  | 22.9±10.3 |
| 24 h   | 52.3±8.0   | 47.2±10.5 | 44.0±9.2  | 39.4±10.6 | 25.4±10.6 |
| 1 week | 54.3±8.6   | 52.2±10.1 | 43.4±10.4 | 40.4±8.9  | 28.6±11.6 |
| 1 month| 51.9±16.3 | 47.2±10.9 | 39.0±15.0 | 36.2±8.5  | 21.7±5.7  |
| 6 months| 48.3±11.7 | 42.9±10.9 | 31.3±8.4  | 25.3±7.1  | 16.7±5.8  |
| 1 year | 39.7±8.5   | 35.9±9.6  | 27.7±6.7  | 24.6±6.2  | 16.9±6.0  |
| MIGF   |      |      |      |      |      |
| Dry    | 67.9±14.4 | 58.1±12.5 | 53.1±11.4 | 48.9±10.2 | 46.5±12.9 |
| 24 h   | 71.6±14.7 | 61.0±12.4 | 57.1±11.3 | 60.7±11.1 | 56.3±14.2 |
| 1 week | 71.9±14.6 | 66.1±12.4 | 61.2±11.5 | 60.7±10.7 | 59.3±15.8 |
| 1 month| 59.3±15.4 | 48.7±12.5 | 41.8±11.5 | 39.5±10.9 | 40.4±10.9 |
| 6 months| 59.7±12.9 | 47.9±7.1  | 42.2±5.9  | 39.0±10.1 | 39.2±4.5  |
| 1 year | 58.8±13.4 | 47.3±4.4  | 40.5±10.7 | 38.4±6.0  | 35.2±8.8  |

Different lowercase letters indicate significant differences in columns for each individual composite (α=0.05). Different uppercase letters indicate significant differences in rows (α=0.05).

did not have any significant effect on UTS at any depth (p>0.05).

The UTS of all RBCs also decreased with depth, more markedly for conventional RBCs, especially CES2 which exhibited a reduction in UTS by more than 50%. Up to 1 week, the UTS of bulk-fill RBCs (BFB, FTB, TEC) at 5 mm was approximately 10–15% lower than at 1 mm, and the values did not differ significantly (p>0.05). However, a few significant differences were observed after 1 month, and all bulk-fill RBCs exhibited significantly lower UTS values at ≥4 mm than at 1 mm after 6 months and 1 year (p<0.05). The UTS of conventional RBCs (BFII, CES2, MIGF) at 5 mm was significantly lower than at 1 mm (p<0.05) under all storage conditions, except for MIGF after 24 h, 1 week and 1 month. After 6 months and 1 year, the UTS at 1 mm was significantly higher (p<0.05) than at ≥4 mm for all conventional RBCs.

Water sorption and solubility

The results of W_m and W_d are shown in Tables 3 and 4, respectively. The W_m as well as W_d of all the tested RBCs increased over time, but the storage period did not significantly affect W_m at the depth of 1 mm and W_d up to 2 mm for any of the materials (p>0.05). For bulk-
fill RBCs, $W_p$ and $W_d$ increased significantly after 6 months at $\geq$4 mm for BFB and $\geq$3 mm for FTB and TEC ($p<0.001$). For conventional RBCs, a significant increase in $W_p$ was observed after 1 month—at depths of $\geq$3 mm for BFII ($p<0.001$) and $\geq$2 mm for CES2 ($p<0.05$ after at 2 mm, $p<0.001$ at $>3$ mm) and MIGF ($p<0.001$). The differences in $W_p$ were less marked—the $W_d$ of BFII was significantly higher compared to 24 h at 4 mm after 1 year ($p<0.05$), the values of CES2 at $\geq$3 mm increased significantly after 1 month ($p<0.05$), and the increase in the $W_d$ of MIGF was significant only at 5 mm after 6 months and 1 year ($p<0.05$).

**DISCUSSION**

Obtaining optimal mechanical properties of RBCs is important for the clinical success of restorations. For light-cured RBCs, this can be achieved by a sufficient light irradiation time and the delivery of an adequate light energy which provide a high degree of conversion. However, their quality of polymerization and hence mechanical properties decrease with depth because light is attenuated while passing through RBCs$^{17,18}$. The curing depth of RBCs can be characterized using various methods. Regional UTS was selected herein, because its evaluation, as they are initially influenced by the amount of unpolymerized monomers and later by degradation$^{22}$. The results of this study revealed that the UTS, $W_p$ and $W_d$ of the tested conventional and bulk-fill RBCs were affected by the long-term water immersion, especially in deeper layers of the specimens. Therefore, the null
The conventional composites BFII and MIGF performed confirmed by the present study — up to the observation α hypothesis was rejected.

Bulk-fill RBCs are claimed to sufficiently polymerize up to 4–5 mm in thickness, while conventional RBCs are recommended to be placed in increments less than 2 mm in thickness. A deeper transmission of the curing light energy enabled by the optimized translucency of bulk-fill RBCs allows photopolymerization in deeper regions, leading to their higher depth of cure\(^{15}\). This was confirmed by the present study — up to the observation after 1 week, the UTS of bulk-fill composites at 5 mm was no less than 85% of the respective value at 1 mm, and there was no significant difference between them. The conventional composites BFII and MIGF performed surprisingly well up to the depth of 4 mm, but all conventional RBCs exhibited a significantly lower UTS at 5 mm compared to 1 mm with the exception of MIGF after 24 h and 1 week. The largest decrease was observed with CES2 whose UTS at 5 mm was approximately half the value at 1 mm, indicating that radiant exposure was not sufficient at this depth. The low quality of polymerization of conventional composites resulting from their application in a 5 mm layer can be seen as a limitation of this study. Firstly, the lower degree of conversion would result in a lower elastic modulus, possibly affecting UTS results. Secondly, conventional composites are clinically placed in increments, so their performance herein has a limited clinical relevance.

The regional UTS of all tested RBCs increased over the first week of water storage compared to the control group in which measurements were performed after 24 h of storage in dark and dry conditions. Generally, mechanical properties of RBCs decrease upon immersion in water\(^{12,18}\), because its absorption leads to polymer swelling and plasticization\(^{14,15}\). Therefore, the increase in UTS was presumably a result of the post-cure polymerization\(^{22,27}\) which compensated for the negative

| Table 4  | Regional water solubility in μg/mm\(^2\) (mean±S.D.) |
|----------|-----------------------------|
|          | 1 mm     | 2 mm     | 3 mm     | 4 mm     | 5 mm     |
| BFB      |          |          |          |          |          |
| 24 h     | 0.8±0.7\(^a\) | 0.7±0.5\(^a\) | 0.8±0.5\(^a\) | 0.8±0.7\(^a\) | 0.9±0.5\(^a\) |
| 1 week   | 0.9±0.5\(^a\) | 0.8±0.8\(^a\) | 0.9±0.7\(^a\) | 0.9±0.5\(^a\) | 0.9±0.7\(^a\) |
| 1 month  | 0.9±0.6\(^a\) | 0.9±0.8\(^a\) | 1.0±0.8\(^a\) | 1.0±0.6\(^a\) | 1.0±0.7\(^a\) |
| 6 months | 1.0±0.7\(^a\) | 1.0±0.4\(^a\) | 1.0±0.7\(^a\) | 3.0±1.1\(^ab\) | 4.1±1.0\(^ab\) |
| 1 year   | 1.1±0.7\(^a\) | 1.0±0.4\(^a\) | 1.1±0.7\(^a\) | 3.1±1.1\(^ab\) | 4.3±1.0\(^ab\) |
| FTB      |          |          |          |          |          |
| 24 h     | 0.6±0.7\(^a\) | 0.7±0.3\(^a\) | 0.7±0.7\(^a\) | 0.7±0.6\(^a\) | 0.7±0.4\(^a\) |
| 1 week   | 0.8±0.8\(^a\) | 0.7±0.6\(^a\) | 0.9±1.0\(^a\) | 0.9±1.1\(^a\) | 0.7±0.8\(^a\) |
| 1 month  | 0.8±0.6\(^a\) | 0.8±0.6\(^a\) | 1.0±1.0\(^a\) | 1.0±1.1\(^a\) | 0.9±0.8\(^a\) |
| 6 months | 0.9±0.8\(^a\) | 0.9±0.5\(^a\) | 3.7±0.4\(^ab\) | 3.2±0.8\(^ab\) | 2.8±0.8\(^ab\) |
| 1 year   | 0.9±0.8\(^a\) | 1.0±0.5\(^a\) | 3.7±0.4\(^ab\) | 3.2±0.8\(^ab\) | 2.9±0.8\(^ab\) |
| TEC      |          |          |          |          |          |
| 24 h     | 0.5±0.3\(^a\) | 0.6±0.7\(^a\) | 0.7±0.9\(^a\) | 0.8±0.8\(^a\) | 0.9±0.9\(^a\) |
| 1 week   | 0.5±0.4\(^a\) | 0.7±0.7\(^a\) | 0.8±1.5\(^a\) | 0.9±1.1\(^a\) | 0.9±1.1\(^a\) |
| 1 month  | 0.6±0.4\(^a\) | 0.8±0.7\(^a\) | 1.0±1.5\(^a\) | 0.9±0.9\(^a\) | 1.3±1.0\(^a\) |
| 6 months | 0.7±0.6\(^a\) | 1.0±0.5\(^a\) | 2.7±0.7\(^ab\) | 2.4±0.8\(^ab\) | 3.1±0.8\(^ab\) |
| 1 year   | 0.9±0.6\(^a\) | 1.5±0.5\(^a\) | 2.9±0.7\(^ab\) | 2.5±0.8\(^ab\) | 3.3±0.8\(^ab\) |
| BFII     |          |          |          |          |          |
| 24 h     | 1.0±1.0\(^a\) | 0.9±0.9\(^a\) | 0.9±0.4\(^a\) | 0.8±0.5\(^a\) | 1.1±0.5\(^a\) |
| 1 week   | 1.0±0.9\(^a\) | 0.8±0.3\(^a\) | 0.9±0.7\(^a\) | 0.9±0.8\(^a\) | 1.1±1.4\(^a\) |
| 1 month  | 1.1±1.1\(^a\) | 1.0±1.0\(^a\) | 1.7±0.8\(^a\) | 1.7±0.8\(^a\) | 1.8±0.9\(^a\) |
| 6 months | 1.1±1.0\(^a\) | 1.1±1.0\(^a\) | 1.8±0.8\(^a\) | 1.7±0.8\(^a\) | 1.9±1.2\(^a\) |
| 1 year   | 1.1±1.0\(^a\) | 1.2±1.1\(^a\) | 1.8±0.8\(^a\) | 1.8±0.9\(^a\) | 2.3±1.9\(^a\) |
| CES2     |          |          |          |          |          |
| 24 h     | 0.8±0.9\(^a\) | 0.9±0.6\(^a\) | 0.8±0.7\(^a\) | 1.0±0.7\(^a\) | 1.0±0.7\(^+\) |
| 1 week   | 0.7±0.8\(^a\) | 0.9±0.6\(^a\) | 0.9±1.4\(^+\) | 0.9±1.2\(^+\) | 1.0±0.9\(^a\) |
| 1 month  | 1.2±0.8\(^a\) | 1.3±1.1\(^a\) | 2.2±0.9\(^+\) | 2.5±1.2\(^+\) | 2.7±1.0\(^+\) |
| 6 months | 1.2±0.8\(^a\) | 1.3±1.3\(^a\) | 2.3±1.0\(^+\) | 2.6±1.2\(^+\) | 2.8±1.0\(^+\) |
| 1 year   | 1.4±0.8\(^a\) | 1.4±1.5\(^ab\) | 2.4±1.0\(^+\) | 2.7±0.8\(^+\) | 2.8±0.8\(^+\) |
| MIGF     |          |          |          |          |          |
| 24 h     | 1.0±0.8\(^a\) | 1.0±0.9\(^a\) | 1.0±1.0\(^a\) | 1.0±0.8\(^a\) | 0.7±0.8\(^a\) |
| 1 week   | 1.0±0.8\(^a\) | 1.5±0.9\(^a\) | 1.3±0.9\(^a\) | 1.1±1.1\(^a\) | 1.2±0.8\(^+\) |
| 1 month  | 1.0±1.2\(^a\) | 1.5±0.9\(^a\) | 2.0±1.0\(^a\) | 1.9±0.4\(^a\) | 1.9±0.6\(^+\) |
| 6 months | 1.1±1.2\(^a\) | 1.5±0.9\(^a\) | 2.2±1.0\(^a\) | 1.9±0.4\(^a\) | 2.0±0.6\(^a\) |
| 1 year   | 1.2±1.2\(^a\) | 1.6±0.9\(^a\) | 2.2±0.9\(^a\) | 1.9±0.5\(^a\) | 2.1±0.6\(^a\) |

Different lowercase letters indicate significant differences in columns for each individual composite (α=0.05). Different uppercase letters indicate significant differences in rows (α=0.05).
effect of absorbed water. The post-cure polymerization was found to continue even after 24 h \(^{25}\), and it was more pronounced in RBCs with a lower initial degree of conversion due to the higher mobility of unreacted monomers and radicals in the polymer network\(^{20}\). Consequently, deeper regions with an insufficient light-activation could benefit from the post-cure polymerization more than shallower regions that are sufficiently photopolymerized. This was most marked for FTB, TEC and MIGF, whose UTS at the depth of 5 mm depth increased over the first week more than UTS at the depth of 1 mm.

The post-cure polymerization could also affect the depth of cure of RBCs. For the bulk-fill RBCs, UTS after 24 h of water storage surpassed 90% of the maximum UTS (obtained at the depth of 1 mm after 1 week of water storage) up to the depth of 2 mm (BFB and TEC) and 3 mm (FTB). While a similar result was observed for FTB after the 1 week-water storage, the depth of cure increased to 4 mm for BFB and 5 mm for TEC, indicating the post-cure polymerization in the deeper regions. On the other hand, the initial depth of cure of conventional RBCs (1 mm) was hardly altered after the 1-week water storage —1 mm for BFII and 2 mm for CES2 and MIGF. Based on these results, we speculate that the post-cure polymerization process plays an important role in obtaining a higher depth of cure in bulk-fill RBCs.

Further water storage beyond 1 week reduced the UTS of all tested RBCs. Given that the UTS values of RBCs are strongly influenced by the polymer structure and the adhesion between the resin matrix and fillers\(^{27,28}\), the reduction of UTS during long-term water storage would be due to the degradation of the polymer network by hydrolysis\(^{15}\) and/or debonding at the filler/matrix interface\(^{39}\). The decrease in UTS was least pronounced at the depth of 1 mm, where sufficient light energy for polymerization can be delivered to the RBCs. In deeper layers, UTS decreased more markedly and was associated with an increase in \(W_{sl}\) and \(W_d\). The \(W_{sl}\) and \(W_d\) of cured RBCs are well-known to increase over the period of water immersion\(^{30,31}\), and their extent is affected by the molecular polarity, the degree of monomer conversion, and the presence of hydroxyl groups capable of hydrogen bonding with water\(^{12}\). The initial \(W_{sl}\) and \(W_d\) can also be attributed to the leaching of unreacted monomers\(^{22}\), but their increase observed in the present study after immersion in water for more than 1 month was presumably caused by the hydrolytic degradation of the resin matrix especially in the deeper regions, where polymerization was not sufficiently initiated by light.

The bulk-fill RBCs FTB and TEC initially exhibited no significant difference in UTS at different depth levels, which is in agreement with previous reports that FTB and TEC could be adequately cured to the depth of 4–5 mm\(^{35}\). However, a significant decrease in UTS was observed after 1 month at the depth of 5 mm for FTB and ≥4 mm for TEC. Given that there was no significant difference in their \(W_{sl}\) and \(W_d\) at this point (except for the \(W_{sl}\) of TEC at 5 mm), the reduction in UTS might be due to the deterioration of filler particles and/or the filler/matrix interface. FTB is a nanofilled RBC utilizing nano-sized silica and zirconia particles, as well as their loosely bound agglomerates (nanoclusters) which were found to be susceptible to deterioration during long-term water storage\(^{6,34}\). As for TEC, the barium silicate glass might be associated with the reduced UTS, as it was found that upon encounter with water, barium was exchanged with the hydrogen ion of water, making the barium silicate glass sensitive to water\(^{55}\). After 6 months and 1 year, the UTS of FTB decreased significantly at depths ≥3 mm. For TEC, 6 months of water storage led to a significant decrease in UTS at ≥2 mm, and the decrease was significant at all depths after 1 year. Additionally, the \(W_{sl}\) and \(W_d\) of FTB and TEC at the depth ≥3 mm increased significantly after 6 months, indicating a hydrolytic degradation of the resin matrix in the deeper regions.

As opposed to FTB and TEC, the bulk-fill RBC BFII exhibited no significant differences in UTS, \(W_{sl}\) and \(W_d\) up to the depth of 3 mm, and the deeper layers were significantly affected only after 6 months and 1 year. Interestingly, an even better outcome was obtained with the conventional RBC BFII, despite its application in a much thicker layer than recommended by the manufacturer. The UTS of BFII decreased non-significantly over the 1-year water storage, its \(W_{sl}\) increased significantly at depths of 3 mm or more after 1 month, and there was no significant difference in its \(W_d\) except for the depth of 4 mm after 1 year. These results might be related to the high filler load in BFB and BFII. Moreover, these two composites utilize a surface pre-reacted glass (S-PRG) filler which consists of three layers—a fluoroaluminosilicate glass core, a pre-reacted glass-ionomer phase on the core surface, and a superficial reinforced layer\(^{36}\). The principal advantage of the S-PRG filler is the increased acid buffering capacity resulting from the release of multiple ions (\(F^-\), \(Al^{3+}\), \(Sr^{2+}\), \(Na^+\), \(BO_3^{3-}\) and \(SiO_2^{4-}\))\(^{70}\). While ion release is usually associated with accelerated hydrolysis, we speculate that the ions released from S-PRG fillers might have buffered the slightly acidic pH of distilled water, thus restraining the hydrolytic degradation of the resin matrix during long-term immersion\(^{39}\) and contributing to the relatively stable UTS, \(W_{sl}\) and \(W_d\) of BFB and BFII.

The other conventional RBCs tested in this study, CES2 and MIGF, were significantly affected by immersion in water for 1 month or more. In the case of CES2 containing barium glass fillers, the effect of water storage combined with increasing depth resulted in very low UTS values. MIGF exhibited a significant decrease in UTS after 1 month, but its values remained stable during further storage. The \(W_{sl}\) of CES2 and MIGF increased significantly after 1 month at all depths except 1 mm, and their \(W_d\) also increased in the deeper layers, although not so markedly. These results indicated that the resin matrix in cured conventional RBC was susceptible to hydrolytic degradation at the depth of 2 mm and more because of poor polymerization, confirming the need to place them in increments less than 2 mm in thickness.
While bulk-fill RBCs performed better than conventional RBCs, the immersion in water for 1 year decreased their UTS at 3 mm to 65–75% of the maximum value measured after 1 week, and UTS values at 4 mm and 5 mm were approximately half the maximum value. Moreover, at the depth of 3 mm or more, the values of $W_{sp}$ increased approximately 5 times and $W_d$ 2–4 times. Indeed, these results represent the worst-case scenario, as beam-shaped micro-specimens tested in this study were fully exposed to water. Under clinical conditions, $W_{sp}$ and thus the degradation of RBCs would not be so intensive in the deep layers, because they are not directly exposed to the oral environment. On the other hand, the storage of bulk specimens could lead to misleading outcomes, because the exposed surfaces would likely exhibit a higher rate of degradation than the unexposed ones. In this aspect, beam-shaped micro-specimens were more suitable, because the same conditions could be achieved for each depth level. Taking into account that the clinical effect would manifest later, the present results suggest that the polymer network of RBCs formed by post-cure polymerization in deeper regions might be susceptible to hydrolytic degradation compared to shallower regions where RBCs are sufficiently activated by light. While further research of mechanical and chemical properties of polymer network formed by post-cure polymerization is required to confirm this speculation, the findings of this study indicate that the incremental placement in <3 mm thick layers should be recommended even for bulk-fill composites when restoring deep cavities.

CONCLUSION

Within the limitations of this study, bulk-fill-RBCs initially exhibited a relatively high UTS even at the depth of 4–5 mm, indicating a quality of polymerization superior to conventional RBCs. However, the UTS of all tested materials deteriorated over the long-term water storage, and their $W_{sp}$ and $W_d$ increased in regions deeper than 2 mm. Therefore, the application of bulk-fill RBCs in layers ≤3 mm should be recommended even for bulk-fill composites when restoring deep cavities.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant Numbers 18K09571 and 19K10106).

REFERENCES

1) Ferracane JL. Resin composite — State of the art. Dent Mater 2011; 27: 29-38.
2) Chandrasekar V, Rudrapati L, Badami V, Tummala M. Incremental techniques in direct composite restoration. J Conserv Dent 2017; 20: 386-391.
3) Finan L, Palin WM, Moskwa N, McGinley EL, Fleming GJ. The influence of irradiation potential on the degree of conversion and mechanical properties of two bulk-fill flowable RBC base materials. Dent Mater 2013; 29: 906-912.
4) Rueggeberg FA. State-of-the-art: Dental photocuring — A review. Dent Mater 2011; 27: 39-52.
5) Fleming GJ, Awan M, Cooper PR, Sloan AJ. The potential of a resin-composite to be cured to a 4mm depth. Dent Mater 2008; 24: 522-529.
6) International Organization for Standardization. ISO 4049 Dentistry — Polymer-based restorative materials, 5th edition, 2019.
7) Moraes LG, Rocha RS, Menegazzo LM, de Araújo EB, Yukimito K, Moraes JC. Infrared spectroscopy: a tool for determination of the degree of conversion in dental composites. J Appl Oral Sci 2008; 16: 145-149.
8) Nayif MM, Nakajima M, Aksornmuang J, Ikeda M, Tagami J. Effect of adhesion to cavity walls on the mechanical properties of resin composites. Dent Mater 2008; 24: 83-89.
9) Moore BK, Platt JA, Borges G, Chu T-MG, Katsilieri I. Depth of cure of dental resin composites: ISO 4049 depth and microhardness of types of materials and shades. Oper Dent 2008; 33: 408-412.
10) Beuschlicher MR, Rueggeberg FA, Wilson RM. Correlation of bottom-to-top surface microhardness and conversion ratios for a variety of resin composite compositions. Oper Dent 2004; 29: 698-704.
11) Idé K, Nakajima M, Hayashi J, Hosaka K, Ikeda M, Shimada Y, et al. Effect of light-curing time on light-cure/post-cure volumetric polymerization shrinkage and regional ultimate tensile strength at different depths of bulk-fill resin composites. Dent Mater J 2019; 38: 621-629.
12) Bastioli C, Romano G, Migliaresi C. Water sorption and mechanical properties of dental composites. Biomaterials 1990; 11: 219-223.
13) Malacarne J, Carvalho RM, de Goes MF, Svizero N, Pashley DH, Tay FR, et al. Water sorption/solubility of dental adhesive resins. Dent Mater 2006; 22: 973-980.
14) Sideridou ID, Karabela MM, Vouvdou E. Dynamic thermomechanical properties and sorption characteristics of two commercial light cured dental resin composites. Dent Mater 2018; 24: 737-743.
15) Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater 2006; 22: 211-222.
16) Nagano D, Nakajima M, Takahashi M, Ikeda M, Hosaka K, Sato K, et al. Effect of water aging of adherend composite on repair bond strength of nanofilled composites. J Adhes Dent 2018; 20: 425-433.
17) dos Santos GB, Alto RVM, Filho HRS, da Silva EM, Felowas CE. Light transmission on dental resin composites. Dent Mater 2008; 24: 571-576.
18) Silikas N, Eliades G, Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. Dent Mater 2000; 16: 292-296.
19) Bucuta S, Ilie N. Light transmittance and micro-mechanical properties of bulk fill vs. conventional resin based composites. Clin Oral Investig 2014; 18: 1991-2000.
20) Nayif MM, Nakajima M, Foxton RM, Tagami J. Bond strength and ultimate tensile strength of resin composite filled into dentine cavity: effect of bulk and incremental filling technique. J Dent 2008; 36: 228-234.
21) Aksornmuang J, Nakajima M, Foxton RM, Tagami J. Mechanical properties and bond strength of dual-cure resin composites to root canal dentin. Dent Mater 2007; 23: 226-234.
22) van Landuyt KL, Nawrot T, Geebelen B, De Munck J, Snauwaert J, Yoshihara K, et al. How much do resin-based dental materials release? A meta-analytical approach. Dent Mater 2011; 27: 723-747.
23) Leung RL, Fan PL, Johnston WM. Post-irradiation polymerization of visible light-activated composite resin. J Dent Res 1983; 62: 363-365.
24) Filo R, Cardash HS. Post-irradiation polymerization of different anterior and posterior visible light-activated resin composites. Dent Mater 1992; 8: 299-304.
25) Par M, Gamulin O, Marovic D, Klaric E, Tarle Z. Raman spectroscopic assessment of degree of conversion of bulk-fill resin composites — changes at 24 hours post cure. Oper Dent 2015; 40: e92-e101.
26) Lovell LG, Newman SM, Bowman CN. The effects of light intensity, temperature, and comonomer composition on the polymerization behavior of dimethacrylate dental resins. J Dent Res 1999; 78: 1469-1476.
27) Yoshida Y, Shirai K, Nakayama Y, Itoh M, Okazaki M, Shintani H, et al. Improved filler-matrix coupling in resin composites. J Dent Res 2002; 81: 270-273.
28) Lin CT, Lee SY, Keh ES, Dong DR, Huang HM, Shih YH. Influence of silanization and filler fraction on aged dental composites. J Oral Rehabil 2000; 27: 919-926.
29) Söderholm KJ, Zigan M, Ragan M, Fischlschweiger W, Bergman M. Hydrolytic degradation of dental composites. J Dent Res 1984; 63: 1248-1254.
30) Eweis AH, Yap AU, Yahya NA. Dynamic analysis of bulk-fill composites: Effect of food-simulating liquids. J Mech Behav Biomed Mater 2017; 74: 183-188.
31) Ortengren U, Andersson F, Elgh U, Terselius B, Karlsson S. Influence of pH and storage time on the sorption and solubility behaviour of three composite resin materials. J Dent 2001; 29: 35-41.
32) Mortier E, Gerolde DA, Jacquot B, Panighi MM. Importance of water sorption and solubility studies for couple bonding agent — resin-based filling material. Oper Dent 2004; 29: 669-676.
33) Tsujimoto A, Barkmeier WW, Takamizawa T, Latta MA, Miyazaki M. Depth of cure, flexural properties and volumetric shrinkage of low and high viscosity bulk-fill gomers and resin composites. Dent Mater J 2017; 36: 205-213.
34) Alnasabi W, Tichy A, Abdou A, Hosaka K, Nakajima M, Tagami J. Effect of water storage and thermocycling on light transmission properties, translucency and refractive index of nanofilled flowable composites. Dent Mater J 2021; 40: 599-605.
35) Tarumi H, Torii M, Tsuchitani Y. Relationship between particle size of barium glass filler and water sorption of light-cured composite resin. Dent Mater J 1995; 14: 37-44.
36) Ito S, Iijima M, Hashimoto M, Tsukamoto N, Mizoguchi I, Saito T. Effects of surface pre-reacted glass-ionomer fillers on mineral induction by phosphoprotein. J Dent 2011; 39: 72-79.
37) Shimizu-Miura M, Inokoshi M, Wada T, Takahashi R, Uo M, Minakuchi S. Basic properties of novel S-PFG filler-containing cement. Dent Mater J 2020; 39: 963-969.