Evaluation of Flowable Resin Composite Surfaces Eroded by Acidic and Alcoholic Drinks

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The purpose of this study was to evaluate the morphological changes of the surfaces of flowable resins eroded by orange juice and alcohol drinks. The tested products were Beautifil Flow BF02 and BF10, Clearfil Majesty LV, Filtek™ Supreme XT Flowable Restorative, Unifil LoFlo Plus and Filtek™ Supreme. Filler percentages of flowable resins were calculated after the latter were incinerated at 750°C. Specimens were shaped into a disk form with a diameter of 10 mm and a thickness of 1 mm. Morphological changes were evaluated for the following types of flowable resin surfaces: polished surface, surfaces eroded by 100% orange juice, wine and whisky. Filler percentages of the tested flowable resins ranged between 42 and 78%. Surface degradation was observed for the specimens immersed in acidic and alcoholic drinks, and it was thought that the lower the filler percentage, the greater was the surface degradation. Decomposition of the matrix resin and fallout of the fillers were observed in flowable resins that eroded with acidic and alcoholic drinks.

Key words: Flowable resin composite, Surface degradation, Alcohol drink

INTRODUCTION

The replacement of lost teeth is usually desired for two primary reasons: esthetics and the restoration of function. Therefore, materials used to restore function must also be esthetically appealing. In addition, the material should be easy for the dentist to use.

In recent years, flowable resins with a lower filler content have been developed. Flowable resins have a far lower viscosity than conventional hybrid resin composites, and they are assumed to have a composite basic composition similar to that of conventional resins.

With resin composites, material properties such as color, cavity adaptability and wear are important for clinical use. For example, in the oral cavity environment, dental cement is immersed in various aqueous solutions, and clinical observations have shown that it undergoes continuous erosion over time.

One of the most important properties that determine the durability of dental materials in the oral cavity is their resistance to dissolution or disintegration. Acid erosion has clinical significance, because acidic conditions can occur orally either due to the ingestion of acidic foods or the degradation of polysaccharides to acids in stagnant areas of the mouth. The current standards for dental cements require the impinging jet erosion test of the materials employed for dental cements. This method evaluates the depth loss of cement in order to quantify the erosion and thus enables material comparisons to be made. This is a slight variation of the method originally proposed by Beech and Bandyopadhyay.

In contrast, orange juice, whisky and cola cause degradation in resin composite materials. The increasing demand for esthetic dentistry has been coupled with a rapid development of new restorative materials. Flowable resin is one of the newly developed esthetic restorative materials, and it is currently being used for dental clinical work as well as in operative dentistry. However, in the complex environment of the oral cavity (with exposure to alcohol, acids, mechanical abrasion and temperature changes), flowable resins are expected to undergo considerable degradation.

An alcoholic and/or acidic environment causes the surface degradation of resin composites. In addition, the surface degradation of resin materials is related to the content of the fillers, distribution of the fillers, composition of the matrix resin, and the effect of silane surface treatment on the fillers.

The purpose of this study was to evaluate the microstructure of the eroded surfaces of flowable resins which were exposed to acidic and alcoholic solutions.

MATERIALS AND METHODS

Materials
Table 1 shows the six flowable resin tested in this study: Beautifil Flow F02 and F10, Clearfil Majesty
Table 1  Materials used in the study

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Main Composition</th>
<th>Type</th>
<th>Filler content (weight%)</th>
<th>Manufacturer</th>
<th>Batch number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beautifil Flow F02</td>
<td>BF02</td>
<td>Bis-GMA, TEGDMA Glass filler, other</td>
<td>Flowable</td>
<td>48.3 (0.01)↑ (54.5)↓</td>
<td>SHOFU INC.</td>
<td>PN 1433</td>
</tr>
<tr>
<td>Beautifil Flow F10</td>
<td>BF10</td>
<td>Bis-GMA, TEGDMA Glass filler, other</td>
<td>Flowable</td>
<td>46.8 (0.01) (53.5)</td>
<td>SHOFU INC.</td>
<td>PN 1463</td>
</tr>
<tr>
<td>Clearfil Majesty LV</td>
<td>MJLV</td>
<td>Barium glass, SiO2-filler TEGDMA, Other</td>
<td>Flowable</td>
<td>78.2 (0.04) (2.01)</td>
<td>Kuraray Medical</td>
<td>00001A</td>
</tr>
<tr>
<td>Filtek TM Supreme XT</td>
<td>FSXT</td>
<td>Bis-GMA, TEGDMA, Dimethacrylate polymer UDMA</td>
<td>Flowable</td>
<td>61.6 (0.12) (65.0)</td>
<td>3M ESPE, MN</td>
<td>6CA</td>
</tr>
<tr>
<td>Restorative Unif LoFlo Plus</td>
<td>ULP</td>
<td>Silica/Zirconia UDMA Fluoroaluminate silicate</td>
<td>Flowable</td>
<td>42.7 (0.12) (63.0)</td>
<td>GC.</td>
<td>310031</td>
</tr>
<tr>
<td>Filtek™ Supreme</td>
<td>FSP</td>
<td>Bis-GMA, Bis-EMA, UDMA, TEGDMA, Silica nanocluster</td>
<td>Paste</td>
<td>75.6 (0.09) (72.5)</td>
<td>3M ESPE, MN U.S.A</td>
<td>3AAJ</td>
</tr>
</tbody>
</table>

Bis-GMA: Bisphenol A glycol dimethacrylate  
TEGDMA: triethylene glycol dimethacrylate  
UDMA: urethane dimethacrylate  
Bis-EMA: ethoxylated bisphenol A glycol dimethacrylate

Table 2  Drinks used in the study

<table>
<thead>
<tr>
<th>Erosion solution</th>
<th>pH</th>
<th>Alcohol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange juice</td>
<td>3.2</td>
<td>–</td>
</tr>
<tr>
<td>(HYP 100, Kirin, Tokyo)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whisky</td>
<td>3.6</td>
<td>40</td>
</tr>
<tr>
<td>(Suntory Old Whisky, Suntory, Japan)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wine</td>
<td>6.2</td>
<td>12</td>
</tr>
<tr>
<td>(Martinys, monteflascone, Italia)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

LV, Filtek™ Supreme Flowable Restorative, Unifil LoFlo Plus and Filtek™ Supreme, a conventional hybrid resin composite serving as a control.

One low pH (100% orange juice) and two alcoholic (wine and whisky) solutions were also used in the study (Table 2).

Weight percentage measurement of fillers

A quantity of 0.3 g of each material was placed in a crucible, and then the samples were incinerated (30 minutes) at the highest temperature of 750°C in an incinerator (AUTO FURNACE EF-I, GC, Tokyo, Japan). The weight percentages of flowable resin fillers were determined from the weight after incineration. Five samples (n=5) of each material were used, and its nominal weight was assigned to the inorganic fillers. This experiment was conducted in accordance with the ISO standard, ISO 4049-1978 E↑.

Specimen preparation for surface observation

A plastic ring mold with internal dimensions of 10 mm diameter and 1 mm height was used to prepare 120 disk-shaped specimens (20 disks per material). The mold with specimen material was held between two glass slides and covered with a transparent polyester strip. The specimens were prepared at room temperature (23±2°C). The materials were polymerized using a visible light curing unit (XL 3000, 3MESPE, MN, USA), with 40-second exposure to each surface of the specimen (top and bottom). The materials were manipulated exactly according to the manufacturers' instructions. All specimen surfaces were ground with #600 to #1200 diamond grinding disks (Struers A/S, Copenhagen, Denmark) and kept in deionized water for 24 hours at a temperature of 37°C. Specimen surfaces at this stage of the experiment were used as standard surfaces. After 14-day immersion in the acidic and alcoholic test solutions, the standard specimens were rinsed for 15 minutes under running water (tap water). In addition, the pH values of the test drinks were checked using a pH test paper (Advantec, Chiba, Japan). Table 2 shows the pH values and alcohol percentages of the test drinks.

Surface roughness (Ra) measurement

Each specimen was dried with absorbent paper, and surface roughness profiles of the top surfaces were
taken using a confocal laser scanning microscope (LSCM 1100, Olympus, Tokyo, Japan). On each evaluated surface, five random traces along its length were performed to assure a linear profile pattern. Baseline surface roughness was obtained by the arithmetic mean of these five readings.

**SEM observation**

All specimens were coated with palladium using a sputter coater (Ion Coater IC-50, Shimadzu, Kyoto, Japan) and examined using a scanning electron microscope (SEM; S-2300, Hitachi, Tokyo, Japan) at an accelerating voltage of 15 kV.

**Statistical analysis**

The mean values for the different groups (surface roughness) were compared using one-way ANOVA and Tukey’s HSD multiple comparison test at a significance level of 0.05. All statistical calculations were performed using a statistical software package (SPSS 10J for Windows, SPSS Japan Inc., Tokyo, Japan).

**RESULTS**

**Weight percentages of the filler content**

Table 1 shows the weight percentages of the resin fillers. They ranged from 42.7% (ULP) to 78.2% (MJLV). For the other tested composite resins, the weight percentages were 46.8% (BF10), 48.3% (BF02), 61.6% (FSXT) and 76.4% (FSP). While the filler contents reported by the manufacturers were shown simultaneously (values that followed the SD values), the given values were about 10 percent higher the measured filler contents in this study.

**Surface roughness**

Under the same experimental conditions, no significant differences in surface roughness (Ra) were found among the standard specimens of the different materials (Table 3). However, for each material, there were significant differences among the specimens exposed to the different beverages, namely, orange juice, wine and whisky (P<0.05). For specimens of the same material that were exposed to wine and whisky, their statistical differences were not large. Among the different test materials, MJLV, FSXT, and FSP showed significant differences from BF02 BF10 and ULP when the specimens were exposed to wine and whisky (P<0.05).

**LSCM observation of surface profiles**

LSCM scanning did not reveal surface roughness in the standard specimens (all A of Figs. 1-1 to 6), and these specimens showed a smooth surface. Specimens B were eroded with orange juice and clearly showed surface roughness (Figs. 1-1, 1-2, 1-3, 1-5). Specimens C were eroded with wine, and showed surface roughness similar to specimen B in each material. Specimens D were eroded with whisky and showed surface roughness similar to specimens B and C in each material (Figs. 1-1, 1-2, 1-3, 1-5). Meanwhile, the surface roughness values of Figs. 1-1 to 1-6 (all B, C, and D thereof) were large when exposed to orange juice, wine or whisky in comparison to the standard specimens. In addition, remarkable surface ruggedness was observed in Figs. 1-1(BF02), 1-2 (BF10) and 1-5 (ULP). Slight surface ruggedness was observed in Fig. 1-3 (MJLV). However, there was almost no shown surface ruggedness in FSXT (Figs. 1-4B, C, and D) or FSP (Figs. 1-6B, C, and D).

**SEM evaluation**

SEM analysis showed smooth surface profiles in the standard specimens. Fallout of the fillers and decomposition of the matrix resin were not shown in each standard specimen (all A of Fig. 2).

Fallout of the fillers and decomposition of the matrix resin were observed on specimens exposed to orange juice, wine and whisky in Figs. 2-1 (BF02; Arrow: filler fallout), 2-2 (BF10), and 2-5 (ULP;
Fig. 1 LSCM images of the flowable resin specimens (Fig. 1-1: BF02; Fig. 1-2: BF10; Fig. 1-3: M1L; Fig. 1-4: FSXT; Fig. 1-5: ULP; Fig. 1-6: FSP). A: standard specimen surface; B: orange juice-eroded surface; C: wine-eroded surface; D: whisky-eroded surface.
Fig. 1-3 MJLV

Fig. 1-4 FSXT

Fig. 1  LSCM images of the flowable resin specimens (Fig. 1-1: BF02; Fig. 1-2: BF10; Fig. 1-3: MJLV; Fig. 1-4: FSXT; Fig. 1-5: ULP; Fig. 1-6: FSP). A: standard specimen surface; B: orange juice-eroded surface; C: wine-eroded surface; D: whisky-eroded surface.
Fig. 1-5 ULP

Fig. 1-6 FSP

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Fig. 2  SEM images of the flowable resin specimens (Fig. 2-1: BF02; Fig. 2-2: BF10; Fig. 2-3: MJLV; Fig. 2-4: FSXT; Fig. 2-5: ULP; Fig. 1-6: FSP). A: standard specimen surface; B: orange juice-eroded surface; C: wine-eroded surface; D: whisky-eroded surface.
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Fig. 2-4 FSXT

Fig. 2 SEM images of the flowable resin specimens (Fig. 2-1: BF02; Fig. 2-2: BF10; Fig. 2-3: MJLV; Fig. 2-4: FSXT; Fig. 2-5: ULP; Fig. 1-6: FSP). A: standard specimen surface; B: orange juice-eroded surface; C: wine-eroded surface; D: whisky-eroded surface.
Fig. 2-5 ULP

Fig. 2-6 FSP

Fig. 2  SEM images of the flowable resin specimens (Fig. 2-1: BF02; Fig. 2-2: BF10; Fig. 2-3: MJLV; Fig. 2-4: FSXT; Fig. 2-5: ULP; Fig. 1-6: FSP).  A: standard specimen surface; B: orange juice-eroded surface; C: wine-eroded surface; D: whisky-eroded surface.
Arrow: decomposition of the matrix and filler fallout). Minor erosion of the surface was observed in MJLV (Fig. 2-3). The surfaces of FSXT (Fig. 2-4) and FSP (Fig. 2-6) (Arrow: nanocluster filler) showed neither the fallout of fillers nor the decomposition of the resin matrices.

**DISCUSSION**

Many foods and drinks (e.g., water, acidic soft drinks, alcoholic drinks, food derivatives) affect the behavior of restorative materials\(^2,^13\). Previous studies have shown that fillers tend to fall out from resin materials\(^6,^9\), and the matrix component decomposes when exposed to low pH environments\(^15,^16\). This surface degradation phenomenon (fallout of fillers and decomposition of the matrix components) of resin materials has also been observed in resin cements\(^15\).

Many soft drinks are acidic and the pH is 3.0 or lower. This means that drinking acidic drinks over a long period and with continuous sipping can erode the tooth enamel — and the resin material as well.

In this study, erosion solutions with pH values of 3.2 (orange juice), 3.6 (wine), and 6.2 (whisky) were chosen for the impinging jet erosion test. As for the alcoholic beverages tested, their alcoholic contents were 12% (wine) and 40% (whisky).

**Surface degradation and its relationship to filler content**

The effect of filler volume on wear resistance follows a linear relationship\(^16,^17\).

In this study, filler content measurement results showed that MJLV had the highest filler content (78.2%) and ULP the lowest (42.7%). The filler contents of BF02, BF10, and ULP were in the lower range (between 42.7 and 48.3% by weight) among these test materials.

Surface degradation was clearly observed on the specimens of BF02, BF10, and ULP that were exposed to alcoholic drinks (wine and whisky) and low pH drinks. In addition, more prominent surface roughness was observed on BF02, BF10, MJLV, and ULP. There were significant differences between these and the standard specimens exposed to orange juice, wine, and whisky (P<0.05; Table 3).

Surface degradation was comparatively slight in MJLV, and almost none was observed in the specimens of FSXT and the control resin composite, FSP. This could be ascribed to the higher filler contents (61.6–78.2%) of these three flowable resins (FSXT, FSP and MJLV) than those of BF02, BF10, and ULP. Therefore, flowable resins of higher filler contents seemed to have a higher resistance to acidic and alcoholic solutions. Meanwhile, wine erosion specimens showed surface degradation similar to the whisky specimens. This was perhaps because the acidity of wine was lower (pH 3.6), as was the alcohol content (12%).

It must be highlighted that it was surprising that FSXT showed no surface degradation in view of its lower filler content (61.6%) in comparison to MJLV (78.2%) and FSP (76.4%). Therefore, apart from filler content, filler properties, filler distribution, and surface treatment of fillers (by silane) were also important factors for resin materials on their erosion resistance to acidic and/or alcoholic solutions.

**Effect of filler distribution on the matrix resin**

Filler fallout in resin materials may not occur easily where there is little exposure of the matrix resin in between fillers (e.g., FSXT and FSP). Decomposition of matrix resin was observed on BF02, BF10 and ULP because these flowable resins showed more exposure of the matrix resin between fillers. That was one of the main weaknesses of BF02, BF10 and ULP. MJLV did not clearly show this characteristic. In contrast, the matrix resin of FSXT was hardly exposed between small and large fillers. This suggested that a relatively high filler loading increased the stability of the resin composite surface.

FSXT contains a unique combination of fillers including zirconia nanofiller particles (diameter: 5–10 nm) and silica nanofiller particles (diameter: 75 nm). In addition, nanocluster fillers (400–600 nm) were formed with zirconia nanofillers and silica nanofillers. Therefore, the higher filler content rate was achieved with three types of particles that were mixed\(^16\). The nanocluster agglomerates acted as a single unit and three types of particles were used, thus enabling a high filler loading and high strength. This served to explain why these flowable resins (FSXT and FSP) showed no surface degradation.

**Surface degradation and its relationship to the matrix resin**

The base resin in the resin polymer was imperfectly polymerized, thus adversely affecting the surface properties\(^9\). Consequently, surface degradation was manifestly shown in flowable resins with lower filler contents (namely, BF02, BF10, and ULP). Amongst which, decomposition of the surface matrix resin was expressly seen in ULP.

Under ideal conditions, the interfacial bond can form a continuous stress distribution between the filler and matrix, provided that the coupling agent has properties intermediate to those of the filler and the matrix. When this occurs, the surface will be more resistant to degradation.

Composite resin has another advantage when used as the coupling agent in dental composites. It protects, at least to some extent, the filler against hydrolytic degradation\(^20,^21\). However, any portion of the organic matrix resin which is insufficiently
polymerized can be dissolved by alcoholic and acidic solutions, and particles can thus easily fall out (B, C, and D of Figs. 2-1 BF02, 2-2 BF10 and 2-5 ULP).

Another possible cause of surface degradation was that the filler and matrix resin were too weakly bonded. This might be related to the surface treatment of fillers, whereby insufficient surface treatment with silane was thought to result in filler erosion.\(^{22,23}\)

In the present study, the morphological differences in filler content, surface roughness and surface microstructure correlated with significant differences in the tested properties of the flowable resins. These differences suggested possible variations in the clinical performance of the tested flowable resin composites.

**CONCLUSION**

Within the limitations of this study, the following conclusions were drawn:

1. A relationship was observed between filler volume and the surface degradation of flowable resins.
2. Distribution density of fillers on resin surface was related to the surface degradation of flowable resins.
3. Surface degradation of flowable resins was also related to the surface treatment of fillers with silane. It was thought that one cause to the fallout of fillers was the insufficient surface treatment of fillers with silane.

**REFERENCES**