Effect of Acetic NaF Solutions on Fluoride-containing Dental Restorative Materials

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The aim of this study was to evaluate the effect of acetic NaF solutions on fluoride-containing restorative materials. As the pH value of solution decreased, the degree of microhardness change in restorative materials increased—regardless of product. Dyract AP (DA) and F2000 (F2) (polyacid-modified composite resins) showed the greatest decrease in microhardness after immersion for three days. Similarly, as the pH value decreased, volumetric weight change (loss) increased in all products. DA and F2 showed the greatest—but similar—weight change in pH 3.5 solution among the products. In terms of color change, most specimens showed a slight color change after immersion for one and three days—regardless of pH value. However, F2 in pH 3.5 solution showed a noticeable color change (ΔE* = 2.1). In terms of surface morphology, specimens in distilled water showed only minor surface modification. However, in pH 3.5 solution, DA and F2 showed randomly propagating cracks, while Solitaire 2 and Tetric Ceram (resin composites) lost many fillers less than 2 μm in size.

Keywords: Fluoride, Acetic acid, Restorative materials

INTRODUCTION

To inhibit caries, the use of fluoride-containing products has become a routine regime in daily life. Fluoride is a well documented anticariogenic agent, which is included in over-the-counter (OTC) products such as toothpastes and mouthrinses at a level of 100-10,000 ppm. Fluoride is also included—in the form of inorganic salts and leachable glasses—in many dental restorative products such as glass ionomer cements, composites (polyacid-modified composite resins), and composite resins. These composite resins have many advantages such as good aesthetics, fluoride release, and antimicrobial action. Of these restorative products, conventional glass ionomer cements release the greatest amount of fluoride, composites the next, and composite resins the least.

The fluoride released has anticariogenic ability by enhancing remineralization. The mechanism is to form a thin layer of fluorapatite on the surface, and thereby inhibit microbial growth and metabolism. Fluoride released from composites or composite resins may reduce the recurrence of caries at the restoration margins and failure of dental restorations. The pH of human saliva in normal situations is generally in the range of 6-8. This range can decrease to 4 after consuming sugar, but it can range from 2 to 11 depending on the foods consumed. However, such changes of oral pH do not persist for a long period because of saliva and plaque buffering. Besides, pH in the oral cavity is also affected by oral acids. Dental plaque on the tooth surface consists of a film of bacteria, some of which produce acids as by-products of their metabolism. Lactic, acetic, and propionic acids are predominantly produced by oral bacteria.

In complicated oral environments, both the remaining fluoride within the teeth after brushing and locally formed acetic acid can interact and produce solutions of differing pH values. The purpose of the present study, therefore, was to evaluate the effect of acetic NaF solutions on fluoride-containing dental restorative materials.

MATERIALS AND METHODS

Resin specimens and test solutions

Table 1 lists the characteristics of the dental materials used in this study. Dyract AP (DA) and F2000 (F2) were composites. Solitaire 2 (S2) and Tetric Ceram (TC) were composite resins. The shade of all these materials was A3. The specimens were polymerized for 40 seconds using a light curing unit (Optilux 501, Kerr, Orange, USA) at 1100 mW/cm² light intensity condition.

To test the fluoride-containing dental materials, two different acetic NaF solutions (0.1%/pH 3.5 and 0.1%/pH 6) were prepared by adding acetic acid to a 0.1% NaF solution. Distilled water (pH 7.8) was used for comparison. To determine the change of fluoride concentration before and after the addition of acetic acid, fluoride concentration was measured from both the 0.1% NaF solution and acetic acid-added NaF solutions of pH 3.5 and 6 using a calibrated fluoride-specific electrode (96-09, Thermo Electron Corp., Beverly, USA) attached to an ion meter (model 720A+, Thermo Electron Corp., Beverly, USA) at an
accuracy of 0.1 ppm. For this purpose, the machine was calibrated from 20 to 50 ppm using a standard fluoride solution. Each measurement was repeated three times under the same conditions after diluting the test solutions.

**Microhardness measurement**

To measure the surface microhardness of specimens, a Vickers hardness tester (MVK H1, Akashi Co., Japan) was used. Twenty-one (three groups of seven specimens were assigned to 0.1%/pH 3.5, 0.1%/pH 6, and distilled water, respectively) specimens of each product were prepared by placing the resin in an acrylic ring mold (7 mm in diameter and 1 mm in depth). The mold was covered with a thin glass slide which was pressed firmly to ensure a flat surface. Specimens were then light-polymerized using a light curing unit under the same curing conditions described above. Next, polymerized specimens were removed from the mold and kept in a dark container for 24 hours prior to taking the measurements. Using a hardness tester, two indentations were made in each specimen at the center of the surface under conditions of a 200-g load and a 10-second dwell time. After measuring microhardness, specimens were immersed in the test solutions at 37°C for one day. After immersion for one day, the specimens were cleaned with running water and the same microhardness measurement was repeated with the same dwell time and load condition. Then, specimens were again immersed in the solutions and additional measurements were repeated at two and three days after immersion. Each repeated measurement was performed 50 μm from the pre-measurement position.

**Weight loss measurement**

To measure the weight loss of the specimens during immersion, specimens (6 mm in diameter and 0.25 mm in thickness) were prepared using the same conditions described above, and kept in a dark container for 24 hours. After that, specimens were dried for 24 hours in a 60°C chamber to remove any moisture or water. Weight of the specimens (n=10 for each solution of each product) was measured using an electronic microbalance (M2-P, Sartorius, Germany; readability: 0.001 mg) before the immersion test. After measuring their initial weights, two groups of five specimens from each product were immersed in each test solution at 37°C for one and three days, respectively. After one and three days, specimens were removed from the solution, cleaned with running water, dried for 24 hours in a 60°C chamber, and their weights measured again. Weight difference between the initial and final weights was then calculated. Volumetric weight loss (g/mm³) was defined as dividing the weight difference by the volume of the tested specimen. A weight difference less than 0.005 mg was assumed to be 0 due to instability of the system and specimen.

**Color change measurement**

To measure the color change that occurred in the specimens after immersion, a Teflon disk (polytetrafluoroethylene, PTFE) was cut and polished. At the center of the Teflon disk, a cylindrical hole (7.1 mm in diameter and 0.7 mm in thickness) was made to set the specimen. In this way, consistency of placing the specimen at the center of the disk was maintained during measurement. Baseline of the UV-VIS-NIR spectrophotometer (CARY 5G, Varian, Victoria, Australia) was corrected by measuring the reflectance of the Teflon disk from 380 to 780 nm. A Teflon disk was chosen as a sample holder because it
could be used to coat the inside of the integrating sphere of the spectrophotometer. After baseline correction, two groups of five specimens from each product were chosen for each test solution. The reflectance of each specimen was measured. After the first reflectance measurement, specimens were immersed in each test solution at 37°C for one and three days, respectively. After one and three days, specimens were removed from the test solution, cleaned, and dried. The same reflectance measurement was performed using the same Teflon disk. Based upon the measured reflectance data, color values on the CIEL*a*b* color coordinate system were evaluated using an internal software of the measurement system. Color difference \( \Delta E^* \) was obtained using the following equation:

\[
\Delta E^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}
\]

where \( \Delta L^* \), \( \Delta a^* \), and \( \Delta b^* \) are the changes in \( L^* \), \( a^* \), and \( b^* \), respectively. Here, \( L^* \) represents the degree of gray and corresponds to a degree of lightness. The parameter \( a^* \) represents the red (for +a* value) - green (for -a* value) axis, whereas \( b^* \) is a parameter in the blue (for b* value) - yellow (for +b* value) axis.

**Surface morphology observation**

To observe surface morphology, specimens were prepared by placing the resin into an acrylic ring mold (7 mm in diameter and 1 mm in depth). The specimens were light-polymerized using the same curing conditions described above, and then kept in a dark container for 24 hours prior to taking the measurements. After 24 hours, the polymerized specimens were polished using SiC paper (#1200) and then ultrasonicated in distilled water for two minutes. The prepared specimens were immersed in each test solution at 37°C for three days. After three days, specimens were removed, cleaned, dried, and gold-coated. Surface observation was performed before and after immersion using a scanning electron microscope (SEM) (S-4200, Hitachi Co., Tokyo, Japan).

**Statistical analysis**

Data acquired for the microhardness and volumetric weight loss measurements were analyzed by two-way ANOVA at 0.05 level of significance. Tukey’s test then followed the multiple comparison test if necessary.

**RESULTS**

**Fluoride and HF concentrations**

Table 2 shows the measured fluoride and estimated hydrofluoric acid (HF) concentrations in solutions of two different pH values. Initial fluoride concentration of a 0.1% NaF solution was 420±5 ppm. The pH value of the 0.1% NaF solution was adjusted to 3.5 and 6 by adding acetic acid. HF concentration was determined by the difference between the fluoride concentration before (1st column in Table 2) and after (3rd column in Table 2) the addition of acetic acid. Free F- ions dissociated from NaF combined with H+ ions, which were dissociated from the acetic acid, and formed HF. The reduction of fluoride after the addition of acetic acid was due to the formation of HF.

**Microhardness**

Table 3 shows the microhardness values of the specimens immersed in different solutions for different days. Change of microhardness in 0.1%/pH 3.5 solution was much greater than the other two solutions - regardless of product. DA and F2 showed the greatest decrease (approximately 20-55% depending on pH value of the test solution) in microhardness after immersion in the solutions for three days. Similarly, TC also showed a great decrease (approximately 17-46%). Although the filler content of TC (vol%: 60) was slightly higher than S2 (vol%: 58), TC showed slightly lower microhardness values than S2. On the other hand, S2 showed the least change in microhardness. On the overall, all the products showed a decrease in microhardness after only one day of immersion. In summary, in terms of microhardness change in all products, pH value and length of immersion were factors that caused statistically significant differences (p<0.001).

**Volumetric weight loss**

Estimated volumetric weight loss (\( \Delta \) g/mm³) of the specimens immersed in different solutions for one and three days are shown in Table 4. As the pH value decreased, the volumetric weight loss increased in all products. DA and F2 showed similar levels of weight change in pH 3.5 solution after one and three days. In all products, most of their weight loss occurred after immersion in the solutions for one day. In terms of volumetric weight loss in most products, pH value and length of immersion were factors that caused statistically significant differences (p<0.001).

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>F (ppm)</th>
<th>HF (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%NaF</td>
<td>3.5</td>
<td>194±4</td>
<td>226</td>
</tr>
<tr>
<td>(F : 420±5 ppm)</td>
<td>6</td>
<td>412±5</td>
<td>8</td>
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</table>

Mean ± SD
Table 3 Microhardness (Hv) of the specimens (n=7) immersed in solutions for different days.

<table>
<thead>
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<th>pH6</th>
<th>pH7.8</th>
<th>pH3.5</th>
<th>pH6</th>
<th>pH7.8</th>
<th>pH3.5</th>
<th>pH6</th>
<th>pH7.8</th>
<th>TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
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<td>49.0</td>
<td>48.7</td>
<td>82.6</td>
<td>84.1</td>
<td>86.1</td>
<td>61.6</td>
<td>65.2</td>
<td>64.1</td>
<td>60.8</td>
</tr>
<tr>
<td>1 day</td>
<td>3.5</td>
<td>1.2</td>
<td>2.7</td>
<td>2.2</td>
<td>3.5</td>
<td>3.2</td>
<td>2.5</td>
<td>1.1</td>
<td>2.2</td>
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<td>2 days</td>
<td>29.5</td>
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<td>40.6</td>
<td>48.6</td>
<td>66.2</td>
<td>74.1</td>
<td>51.4</td>
<td>57.0</td>
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<tr>
<td>3 days</td>
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<td>1.7</td>
<td>3.6</td>
<td>2.8</td>
<td>2.3</td>
<td>2.6</td>
<td>2.7</td>
<td>2.9</td>
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<td>1.7</td>
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<td>2.1</td>
<td>1.0</td>
<td>2.5</td>
<td>2.6</td>
<td>1.2</td>
<td>51.4</td>
<td>3.4</td>
<td>1.2</td>
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<tr>
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<td>2.3</td>
<td>1.9</td>
<td>3.5</td>
<td>2.3</td>
<td>2.4</td>
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<td>2.3</td>
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p-values:

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<th>pH7.8</th>
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<tbody>
<tr>
<td>DA</td>
<td>3.5</td>
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<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
</tr>
<tr>
<td>F2</td>
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<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
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<tr>
<td>S2</td>
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<td>6</td>
<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
</tr>
<tr>
<td>TC</td>
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<td>6</td>
<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Mean ± SD

Table 4 Volumetric weight loss (Da mm) of the specimens (n=5) after immersion in solutions for 1 and 3 days.

<table>
<thead>
<tr>
<th>pH</th>
<th>Da 1</th>
<th>Da 3</th>
<th>p-values</th>
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<tbody>
<tr>
<td>pH3.5</td>
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<td>pH6</td>
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<td>0.001</td>
</tr>
<tr>
<td>pH7.8</td>
<td>3.0</td>
<td>6.1</td>
<td>0.001</td>
</tr>
<tr>
<td>DA</td>
<td>3.5</td>
<td>6.8</td>
<td>0.001</td>
</tr>
<tr>
<td>F2</td>
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<td>13.7</td>
<td>0.001</td>
</tr>
<tr>
<td>S2</td>
<td>3.5</td>
<td>6.8</td>
<td>0.001</td>
</tr>
<tr>
<td>TC</td>
<td>3.5</td>
<td>6.8</td>
<td>0.001</td>
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</tbody>
</table>

p-values:

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<thead>
<tr>
<th></th>
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<th>pH7.8</th>
<th>pH3.5</th>
<th>pH7.8</th>
<th>pH3.5</th>
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<tr>
<td>DA</td>
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<td>7.8</td>
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<td>7.8</td>
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<td>7.8</td>
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<tr>
<td>F2</td>
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<td>S2</td>
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<tr>
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<td>6</td>
<td>7.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Mean ± SD

Table 5 Color difference of the specimens after immersion in solutions for 1 and 3 days.

<table>
<thead>
<tr>
<th>pH</th>
<th>Da 1</th>
<th>Da 3</th>
<th>p-values</th>
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<tbody>
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</tr>
<tr>
<td>3.5</td>
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</tr>
<tr>
<td>3.5</td>
<td>6</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

Data are presented as mean values.

*p-Values as follows: Da 1: Color difference for 1 day.
Da 3: Color difference for 3 days.

*Statistically significant difference on pH values is shown by superscript letters A, B, C. Same letters or numbers are not significantly different by Tukey’s multiple comparison test at significance level of 0.05.

*On p-values, the letters , , and denote pH values, days in solutions, and the interaction between pH values and days solutions, respectively.
Color change
Among the products, TC was the most yellowish. Color change of the specimens was evaluated using CIE *L* *a*b* color values. After immersion for one and three days, most specimens showed a slight color change regardless of pH value of the solution. F2, on the other hand, showed a noticeable color change after immersing in pH 3.5 solution for three days (Table 5).

Surface morphology
Figures 1-4 show the surface morphology of specimens before and after immersion in different solutions for three days. Specimens immersed in distilled
water showed only minor surface modification. In pH 6 solution, some fillers less than 1 μm in DA and TC were missing. Macrofillers in F2 were detached from the resin matrix. In pH 3.5 solution, DA and F2 showed randomly propagating cracks. New synthetic substance was found on the surface. In DA, it looked like a gathering of scales, whereas in F2 it looked like flower buds. In S2 and TC, many fillers less than 2 μm were missing. However, no cracks and no new synthetic substances were found on the surface.

Fig. 2 Surface morphology of F2 after immersion in solutions for 3 days, where a: control; b: pH 7.8; c: pH 6; d: pH 3.5 at ×5000 magnification; e: pH 3.5 at ×500 magnification.
DISCUSSION
Currently available fluoride-releasing dental restorative materials contain fluoride in various forms such as inorganic salts, leachable glasses, or organic fluoride. The tested specimens contained similar filler elements such as Ba, Al, F, and Si with different filler contents (vol%) ranging from 47 to 63%. DA contained strontium in the form of SrF₂. This soluble strontium fluoride enhances fluoride release, but it adversely affects the mechanical properties. S2 was a new substitution of Solitaire. In order to enhance the mechanical properties, S2 did not contain SrF₂. However, this would adversely affect the

Fig. 3 Surface morphology of S2 after immersion in solutions for 3 days, where a: control; b: pH 7.8; c: pH 6; d: pH 3.5 at x5000 magnification; e: pH 3.5 at x500 magnification.
release of fluoride. F2 contained the greatest amount of fillers among the tested specimens. TC contained YbF\(_3\) to increase fluoride release and radiopacity. However, the solubility of YbF\(_3\) relies on pH value\(^{19,20}\). With lactate buffer and water, the solubility of YbF\(_3\) was so low that any change on the surface could not be identified.

Dental caries is one of the most commonly occurring oral diseases. The process of caries is initiated by oral bacteria which reside on the film of dental plaque. Oral bacteria produce acids when they metabolize fermentable carbohydrates\(^{17}\). To prevent caries, fluoride-containing oral hygiene products such as toothpastes or dental rinses are popularly in use.

Fig. 4 Surface morphology of TC after immersion in solutions for 3 days, where a: control; b: pH 7.8; c: pH 6; d: pH 3.5 at \(\times5000\) magnification; e: pH 3.5 at \(\times500\) magnification.
These products contain fluoride at a level of 100-10,000 ppm. The fluoride released from these products can be present in the oral fluid or on the plaque on tooth surface. Fluoride can inhibit bacterial metabolism by forming HF molecules when plaque is acidified\(^\text{21}\). In such complicated oral situations and in the presence of acetic acid, even a small quantity of fluoride can induce the following reaction:

\[
\text{NaF} + \text{CH}_3\text{COOH} \rightarrow \text{HF} + \text{CH}_3\text{COONa}
\]

Acetic acid is one of the acids most commonly produced by oral bacteria. The formed HF concentration in 0.1% acetic NaF solutions of pH 3.5 and 6 were 226 ppm and 8 ppm respectively. However, the concentration could be changed by the fluoride released from the tested products.

Immersed specimens in the solutions showed different degrees of microhardness decrease depending on the product. DA and F2 showed more than 50% decrease of microhardness after immersion for three days. For DA, the weakening of its surface hardness might be related to the enhanced release of fluoride from SrF\(_2\) and its lowest filler content among the tested specimens. For F2, the great decrease in microhardness might also be partly related to the filler content - which was the highest among the specimens. Further, as seen in SEM images, F2 also contained the biggest fillers among the specimens. When put together, the highest filler content and biggest size might further enhance fluoride release. However, it is generally considered that the smaller the filler size, the greater is the fluoride release because the smaller the filler size, the larger is the specific surface area of filler. As a result, weakness of the surface can be expected. Moreover, since F2 contained hydrophilic monomers such as CDMA and GDMA, water absorption of the resin matrix was enhanced and solubility of the glass fillers could be affected. Taken together, these characteristics of F2 would lead to its greatest decrease in microhardness and higher weight loss.

S2 was a new, improvised form of Solitaire. The exclusion of SrF\(_2\) in S2 delayed the weakness in microhardness after immersion\(^\text{20}\). As a result, S2 showed the least decrease in microhardness after immersion. As for TC, its decrease in microhardness after immersion might be related to the loss of fillers and the hydrophilic nature of the monomer (Bis-GMA). Although TC had very low solubility in water, deterioration of surface integrity due to formed pores and absorption of solution - and thereby subsequent chemical softening of the surface - might weaken the surface hardness. In S2, a similar loss of fillers was observed but a lower decrease in microhardness was detected. Such inconsistencies in the decrease of microhardness might stem from the differences of the included fillers and monomers. Since water makes a surface soft and weak, considerable decrease in microhardness of specimens immersed in distilled water would therefore seem natural. Likewise, specimens immersed in a solution of 0.1%/pH 6 yielded similar or slightly lower microhardness values than specimens immersed in distilled water. This was largely because these two solutions did not differ much in pH value.

DA and F2 showed the greatest volumetric weight loss after one and three days. Such great loss might be related to the greatest decrease in microhardness of these products. As for TC, its lowest volumetric weight loss might be related to the inclusion of YbF\(_3\). Since the solubility of YbF\(_3\) in water is very low, TC could have thus exhibited the least weight loss even though it contained the second greatest amount of filler. It should be mentioned that density of fillers also affects weight change if the contained fillers are different. Furthermore, volumetric weight loss was also influenced by the pH value. As the pH value was lowered, the weight loss increased. It should be highlighted that at lower pH value, there would be a greater increase in the concentration of formed HF, which meant a greater influence exerted by the increased HF. Then, as fluoride release from compomer products could be much greater than that of composite resin products\(^\text{16}\), this led to DA and F2 showing much greater weight loss.

According to CIE\(L^*a^*b^*\) color values, specimens of the same shade A3 showed similar \(L^*\) and \(a^*\) values. However, due to high \(b^*\) values in S2 and TC, they looked slightly more yellowish than the other specimens. In dental restorative materials of the same shade number, such shade inconsistencies are common\(^\text{31}\). In the present study, color changes were not always singularly influenced by the pH value of the solution. Relatively high color difference in DA and F2 after three days might be partly due to the formation of new synthetic substance on the surface. According to SEM observation, the new substances showed slightly different lightness characteristics compared to the base color. Such difference in lightness may thus affect the resultant color of a material. In other words, the color and reflectance of the new synthetic substances affected the resultant color of the specimens after immersion.

Concerning surface deterioration, several factors could be involved. To begin with, HF was a strong acid that could even etch porcelain - thus it could dissolve the fillers contained in the composite resins\(^\text{20}\). At the same time, water in the test solutions could be absorbed into the fillers and/or resin matrix depending on the hydrophilicity. Absorbed water then makes the filler surface soft and expands the fillers. Since fillers have different size, volume,
and water absorption capacity, the resultant expansion of the fillers would not be the same. As a result, large fillers in DA and F2 were detached from the resin matrix. Likewise, abundant amounts of fillers in S2 and TC were missing too. However, it was not clear whether they were completely dissolved or just peeled off.

The interaction of fluoride-containing restorative materials with an acetic NaF solution for three days could be considered a long period of time in comparison with the mere several minutes of daily oral hygiene activity. As such, in the latter situation, fluoride remains in the oral cavity for only a few minutes. The observed degradation of physical properties in the present study might not be critical to the longevity of dental restorative materials. However, since individuals differ in dietary habits and use frequency of fluoride-containing oral hygiene products, it would not be a simple straightforward task to evaluate the possibility and likelihood of clinical problems arising from these test solutions.

CONCLUSIONS

Properties of the tested fluoride-containing composite resins were affected by the difference in pH value of the acetic NaF solutions. As the pH value decreased, the microhardness of specimens decreased regardless of product. Among the products, DA and F2 (compomers) showed the greatest decrease after immersion for three days. Similarly, volumetric weight loss increased as the pH value decreased. The change was maximum in 0.1%/pH 3.5 solution regardless of product. In terms of color change, most specimens showed a slight color change regardless of pH values, except for F2 in pH 3.5 solution. Otherwise, on the overall, specimens showed relatively stable color in the acetic NaF solutions. In terms of surface morphology, surface modification became apparent as pH value decreased. In pH 3.5 solution, DA and F2 showed randomly propagating cracks. On the other hand, abundant amounts of fillers were missing in S2 and TC.

REFERENCES