

Analysis of Etching of Tooth-coloured Restoratives by Different Acidulating Systems in Topical Fluoride Gels

Kasmawati Mokhtar^{1*} and John McIntyre²

¹School of Dental Sciences, Universiti Sains Malaysia,
16150 Kubang Kerian, Kelantan, Malaysia

²School of Dentistry, Colgate Australia Clinical Dental Research Centre,
Adelaide University, 5005 South Australia

*Corresponding author: hidayah@kb.usm.my

Abstract: *The aims of this study were to determine the etching effects of acidulated fluoride gels on high-glass-content restorations and to compare these effects with different acidulating systems. Samples of KetacFil, Fuji IX, Z100 and porcelain were separately submerged into either test solutions of 1.23% acidulated fluoride gel (APF) or solutions of the individual acidic components of APF (HF or H₃PO₄) combined with fluoride ions for 1–20 min at 37°C. Subsequently, the Fuji IX samples were exposed to the potential alternative acidulating solutions (polyacrylic, malic, maleic and tartaric acids) for similar time periods and assessed for roughness using profilometry and/or Scanning Electron Microscopy. The results showed that the GICs were most rapidly and extensively etched by the APF solutions. However, porcelain was etched less rapidly and Z100 showed no etching. Of the acidulated fluoride solutions tested, malic and maleic acids showed the greatest etching effect on Fuji IX followed by APF, HFF, tartaric acid, PAA and HPF. In conclusion, the acidulating system containing ortho-phosphoric acid showed the least rapid etching effects, although these effects were still a concern with long term exposure.*

Keywords: acidulated fluoride gels, etching, GIC, porcelain, alternative acidulating systems

1. INTRODUCTION

A number of previous studies have explored the potential of the traditional acidulated fluoride gel (APF), as developed initially by Brudevold¹ to etch those restorative materials that have a high glass or quartz content. These materials include the traditional Glass Ionomer Cements (GICs), certain resin modified GICs (RMGICs) and even certain quartz-filled resin composites (CRs).^{2–5} Dental porcelain is also readily etched by the repetitive use of the traditional APF gels.^{6,7} These studies have led to a substantial reduction in use of these acidulated gels by dental clinicians.

However, there is also evidence of the superiority of APF gels over neutral fluoride gels containing similar concentrations of fluoride ions with respect to the uptake and penetration depth of fluoride ions into enamel⁸ and in their ability to protect against highly acidic challenges to tooth surface enamel.^{9,10} For this reason, it was necessary to first analyse which components of the traditional APF gels caused the greatest etching and, second, to determine how the formula might be best modified to reduce the etching effect.

The formula to prepare a traditional 1.23% APF solution, as reported by Nikiforuk,¹¹ comprises a mixture of ortho-phosphoric acid (H_3PO_4), hydrofluoric acid (HF) and sodium fluoride (NaF). Thus, the degree of etching caused by each of the two acids must be tested individually and compared to the combination of both acids. It was also necessary to test a number of potential alternative acidulating systems for their comparative ability to cause etching of restorative materials when combined with the fluoride ion.

To achieve these objectives, a first test was carried out to determine which dental materials among traditional GICs, a quartz filled resin composite and dental porcelain showed the greatest degree of surface etching when exposed to a traditional APF 1.23% solution. The second test was to compare the degree of etching caused by the APF 1.23% solution to the etching caused by its component acidic solutions on the material that showed the greatest susceptibility to etching. This test was followed by testing five potential alternative acidulating solutions that were combined with the same concentration of fluoride ion to determine the etching abilities. It was hoped that this information would indicate possible modifications to the acidulating systems in acidulated fluoride gels to reduce the degree of etching.

2. EXPERIMENTAL

2.1 Materials to be Tested for Etching Susceptibility

The initial study was carried out using the following dental materials:

- (i) KetacFil Plus (3M ESPE, USA)
- (ii) Fuji IX Fast (GC Corp., Japan)
- (iii) Z100 (3M ESPE, USA)
- (iv) Fired dental porcelain (tooth crowns made from Duceram porcelain powder, Ducera, Germany)

Both KetacFil Plus and Fuji IX Fast were representative of the more traditional Glass Ionomer Cements (GICs). The Resin Composite (CR) Z100 was selected

because it contains quartz, which has a core structure and composition similar to those of glass and was thus considered to be susceptible to etching by APF gels.

2.2 Preparation of Testing Materials

As the plastic restorative materials were to be analysed using a profilometer, a flat surface measuring at least 10 mm across was necessary to form a flat disc of set material. This was achieved using brass washers that were 1.5 mm deep, whereas the central orifice had been widened to 12 mm.

A polyacetate strip was placed on a glass slab, and three washers were placed on the strip. Each restorative material was mixed according to the manufacturer's instructions and placed in excess into the central orifice of a washer. Another polyacetate strip was placed on the sample, a second glass slab was placed on top of the strip and hand pressure was applied to press the materials to achieve a flat, smooth surface for both GICs and Z100. The GIC samples were allowed to set for seven minutes, whereas the pressed specimens of Z100 were light-activated on both sides for 20 sec using a Visilux™2 activator (3M, St. Paul, Germany). Each washer was clearly labelled with the appropriate code for the content material. The same procedure was repeated until 24 samples of each material were prepared, labelled and stored in a high-humidity humidior.

The porcelain samples were composed of porcelain slabs that were made from Duceram Porcelain powder (Ducera, Germany) and were sectioned from crowns. The porcelain crowns were fired at temperatures ranging from 890°C–990°C in a porcelain furnace. Only specimens with no crazing and high glaze were selected for this study. Unfortunately, due to their concave surface structure, the surface roughness of the porcelain samples could not be measured using the profilometer. Therefore, Scanning Electron Microscopy (SEM) was used to assess visually the surface roughness of both the porcelain samples and some of the plastic material samples to compare the changes in the surface roughness with etching.

2.3 Preparation of APF and the Component Acidic Test Solutions

As stated previously, a traditional 1.23% APF gel comprises a solution of ortho-phosphoric acid (H_3PO_4), hydrofluoric acid (HF) and sodium fluoride (NaF) in concentrations described by Nikiforuk,¹¹ resulting in a pH of 3.2–3.5. A thickener, i.e., xanthan gum, is added to this mixture to convert the solution to a gel form to facilitate its use and retention on the applied surfaces. As it would be difficult to work with a gel form in terms of problems with its removal from the specimens without damage to the delicate surface structures, only the solutions of

the APF and its components without the thickener, as described by Nikiforuk, were used in this investigation.

Three specific test solutions were prepared: the first solution contained all components of the 1.23% APF gels in their original concentrations, the second contained only HF and NaF and the third contained only H₃PO₄ and NaF. The precise compositions of these solutions were as follows:

- (i) 20 g NaF + 6.3 ml concentrated H₃PO₄ (85% reagent grade) + 5.9 ml concentrated HF (50% reagent grade) + deionised distilled water (DDW) to make 1 litre of solution (pH 3.5), labelled APF.
- (ii) 20 g NaF + 6.3 ml H₃PO₄ + DDW to 1 litre (pH 5.09), labelled HPF.
- (iii) 20 g NaF + 5.9 ml HF + DDW to 1 litre (pH 4.96), labelled HFF.

All prepared solutions were stored in sealed polyethylene containers.

2.4 Selection and Preparation of Potential Alternative Acidulating Systems

The requirement for such acids was mainly their safety for use in the oral cavity and their lack of toxicity to humans. Those chosen were either weak organic acids with two carboxylic acid groups, e.g., tartaric, malic, maleic or long chain acids used in dental materials, e.g., polyacrylic acid. Solutions of these acids were prepared as follows:

2.4.1 Polyacrylic acid (PAA) solution

Polyacrylic acid powder (Aldrich Chemical Coy, Wisconsin, USA) was added to a 100-ml beaker containing 95 ml DDW and 2 g NaF powder and was gently stirred, while the pH was constantly measured using a previously calibrated pH meter (Eutech Instrument). As the pH decreased slowly, forming an increasingly viscous solution, only solutions at pH 4 and 4.5 were used. When the pH reached these pH levels, the beakers were weighed to determine the weight of PAA powder that was added. A pH of 4.5 was obtained after 4.2 g PAA powder was added, and a pH of 4.0 was obtained after 6.6 g of PAA powder was added. The molecular weight (MW) of the PAA powder was estimated to be 750,000.

2.4.2 Tartaric acid (TA) solution

To prepare tartaric acid, 11.6 g of tartaric acid powder and 2 g of NaF were added to 100 ml of DDW, and the solution was thoroughly mixed until all

the powders had dissolved. The pH of the solution was 3.5, and it was kept in a polyethylene bottle for three days before used.

2.4.3 Malic acid solution

The malic acid solution was prepared as described for the PAA solutions above. DL-Malic acid powder (pKa 3.4, MW = 134) was continuously added to DDW and stirred until completely dissolved, and 11.4 g malic acid was added to a final volume of 100 ml to obtain the required pH of 3.5.

2.4.4 Maleic acid solution

The maleic acid solution was prepared using the same method as for malic acid with the aim to reach a pH of 3.5. However, problems arose with the maleic acid solution because the solution became saturated before the pH 3.5 was achieved, resulting in the formation of crystals in the solution. The procedures were repeated several times with the same result; therefore, the solution was employed with some undissolved crystals still present. Dissolving 7.2 g of maleic acid powder resulted in a pH of 3.5.

2.5 Assessment of Surface Roughness Using Profilometry

A profilometer (Surftest III, Mitutoyo, Japan) was used to measure the Ra values (average surface roughness) on the surface of the material discs following increasing periods of exposure to the acidulated systems. The discs of each material sample were temporarily adhered to a glass slab to remain stable during the measurement. The graphs representing an amplification of the surface roughness profiles over a 10-mm distance were used as follows to determine the Ra values in μm .

Ten sites of peaks and valleys from the roughness profiles were carefully chosen on the graph paper, and the depth of each was measured in mm. The mean depth values (in mm) were calculated and subsequently converted into μm based on the roughness data from the calibration plate using the formula:

$$\text{Ra} = \frac{\text{mean roughness value of a sample (mm)}}{\text{roughness value of the calibration plate (mm)}} \times 2.9 \mu\text{m}.$$

2.6 Assessment of Surface Roughness Using Scanning Electron Microscopy (SEM)

SEM analysis was carried out on both the control and test sections of the porcelain slabs and on selected samples of all three plastic test materials to visualise the degree of roughness represented by each Ra reading for the plastic materials.

The samples were prepared for the SEM analysis by being dehydrated and mounted on metal stubs prior to coating with gold and carbon. As expected, the GICs showed considerable cracking due to the dehydration; therefore, efforts were made to exclude the cracks when viewing these samples under SEM. A Philips XL 30 Scanning Electron Microscope (Philips, Eindhoven, Switzerland) was operated at 10 kV energy level, and the sample surfaces were viewed at magnifications of 5000× and 10,000×.

The differing patterns of etching between the GICs and porcelain present a difficulty in determining a ranking for comparison. Hence, the times at which the first signs of initial etching damage appeared and the subsequent levels of damage over prolonged exposure periods were chosen as the method of comparison for this study.

2.7 Testing Methods

2.7.1 Determining relative susceptibility of the selected dental materials to APF and component solutions

Three groups of eight washers of each of the three materials, KetacFil, Fuji IX and Z100, and eight samples of fired porcelain were selected for this study. One sample of each of the plastic and porcelain materials was retained as a background control specimen. The remaining samples were placed on separate sample holders, which were subsequently submerged into 25 ml of the test solutions APF, HFF and HPF in separate sealed polyethylene containers (4.3 × 5.3 cm) and maintained at 37°C.

A washer of each plastic material and a porcelain slab were removed after 1, 2, 3, 4, 5, 10 and 20 min of exposure to the test solution, washed in DDW, lightly dried, labelled and stored in the high humidity humidior until the surface roughness was tested.

The Ra values were assessed for each washer of plastic material, where each washer represented either the control or a sequential period of immersion. Each Ra value was the mean of ten sites along the roughness graphs. SEM

micrographs were taken of each porcelain slab and of three representative sections of each of the plastic material samples.

2.7.2 Determining the comparative etching ability of APF and its component solutions and those of the alternative acidulating systems on Fuji IX

As described below, among the four test materials, Fuji IX and KetacFil were found to be etched most rapidly and severely by the APF solution (see Results, Figure 1). Fuji IX was accordingly selected as the material for the main study.

Eight groups of five samples of Fuji IX were selected, and their Ra values were determined. These specimens were subsequently exposed to the APF and component solutions, as well as the five alternative acidulating solutions, for exposure periods of 1, 2, 4, 10 and 20 minutes, with the Ra value being determined for each sample following each increment of the exposure time. The resultant Ra values were the means of the eight samples with the same exposure time.

3. RESULTS AND DISCUSSION

3.1 Determining Comparative Susceptibility of Selected Materials to APF and its Component Solutions

Figure 1 shows the degrees of etching by the APF and component solutions as the Ra values (μm) above background (control) levels over time for the different plastic materials. This data indicated that Z100 showed minimal etching even after 20 min of exposure. The level of etching was comparable between Fuji IX and KetacFil, although the etching patterns changed with time, as was particularly evident with Fuji IX. These results indicated a likely surface dissolution of the matrix and probable loss of filler, resulting in fluctuating patterns of etching of the remnant material. These results pointed to the need to focus on the early changes in roughness and the time at which they occurred as the main indicators of the degree of etching for comparative purposes.

Figure 2 shows the changing pattern of etching, as observed by SEM analysis in the Fuji IX, Z100 and porcelain samples over time of exposure. Even though the patterns of the surface change vary among the materials, the degree of change and time at which it occurred also indicate that the traditional GICs exhibited the greatest degree of etching damage. Porcelain exhibited etching damage after four minutes of exposure and severe etching damage after 10 min.

However, Fuji IX exhibited marked etching damage after one minute of exposure to the same acids and extremely severe damage by 10 min. These results confirm what has been noted anecdotally by dental clinicians and are not surprising.

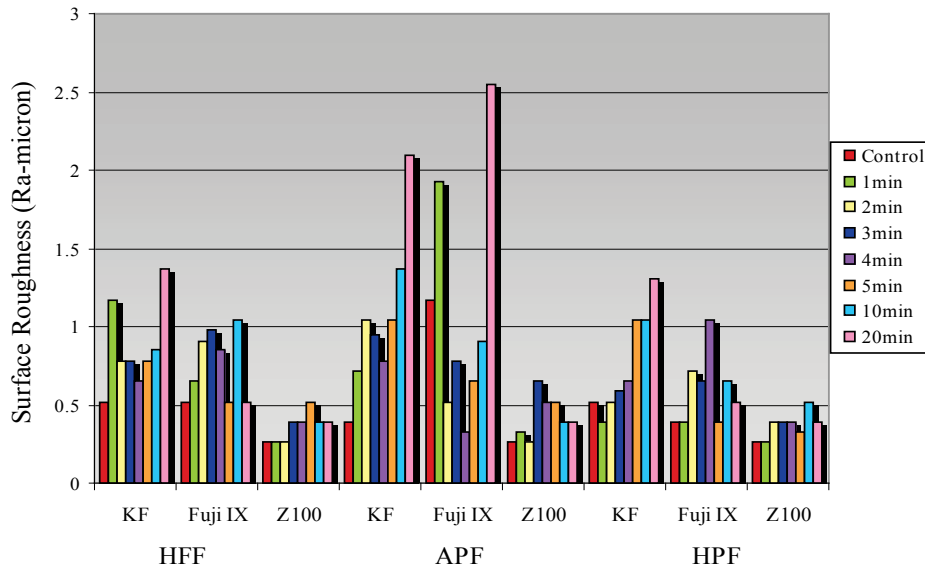


Figure 1: Etching effects of APF solution and its components on tooth-coloured restorative materials as shown by surface roughness (Ra) values in μm for comparative periods of time, including error bars.

Although a wide degree of variability was evident from the profilometer studies, the results pointed to an overall tendency for the HFF component of the APF solutions to contribute most to the etching potential. The phosphoric acid component appeared to take extra time for its etching potential to become fully effective. The difference in pH of the HFF and HPF solutions, as compared to the combined APF solution (approximately pH 5 compared to pH 3.5 for the APF solution), may have contributed to the overall reduced etching effect by the component solutions compared with the combined APF.

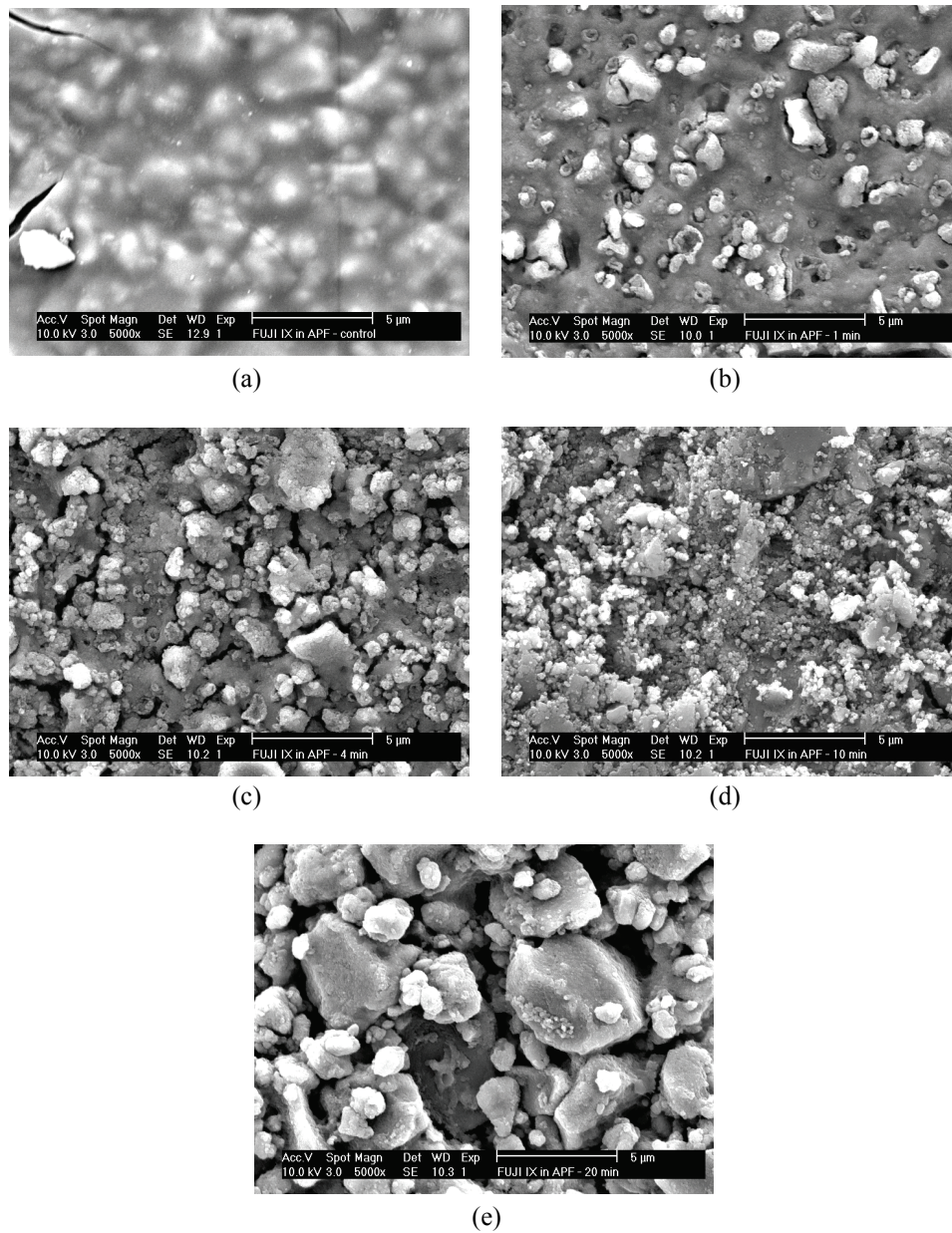


Figure 2: SEM micrographs of Fuji IX (Fig. 2a–e) and porcelain (Fig. 2f–k) surfaces following exposure to APF solution for comparative periods of time; (a) Fuji IX baseline, (b) after 1 min, (c) after 4 mins, (d) after 10 mins, (e) after 20 mins, (f) porcelain after 1 min, (g) after 4 mins, (h) after 10 mins, (i) after 20 mins, (j) Z100 after 5 mins, (k) after 10 mins (5000x for Fuji IX; 10,000x for porcelain and Z100). (continued on next page)

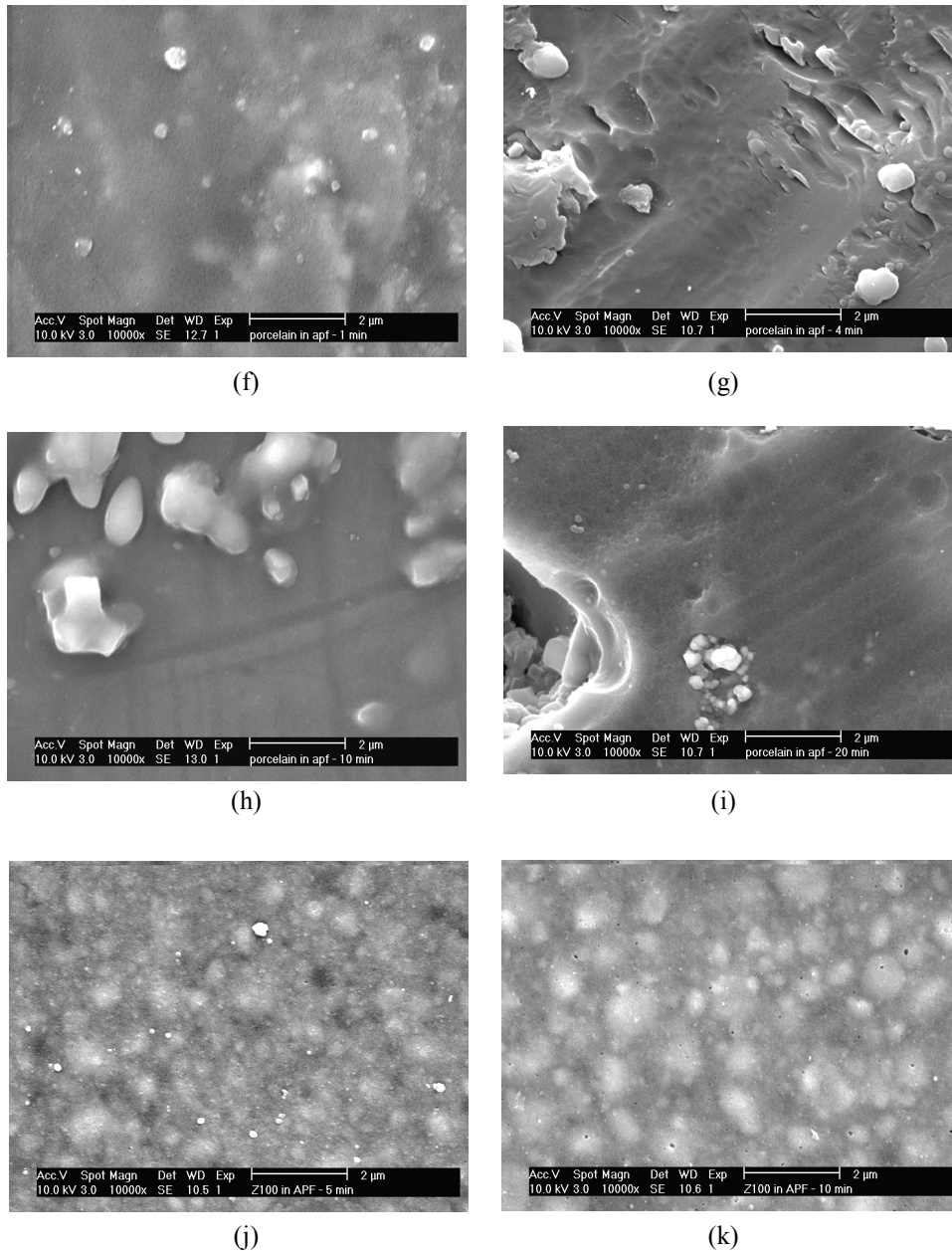


Figure 2: (continued)

3.2 Comparative Degrees of Etching of Fuji IX by APF, HFF and HPF Solutions, and Testing the Alternative Etching Systems above Background Roughness Levels using a Profilometer

Figure 3 shows the increase in roughness of the Fuji IX samples above background levels using the profilometer analysis after exposure to the APF, HFF and HPF solutions for 1, 2, 4, 10 and 20 min.

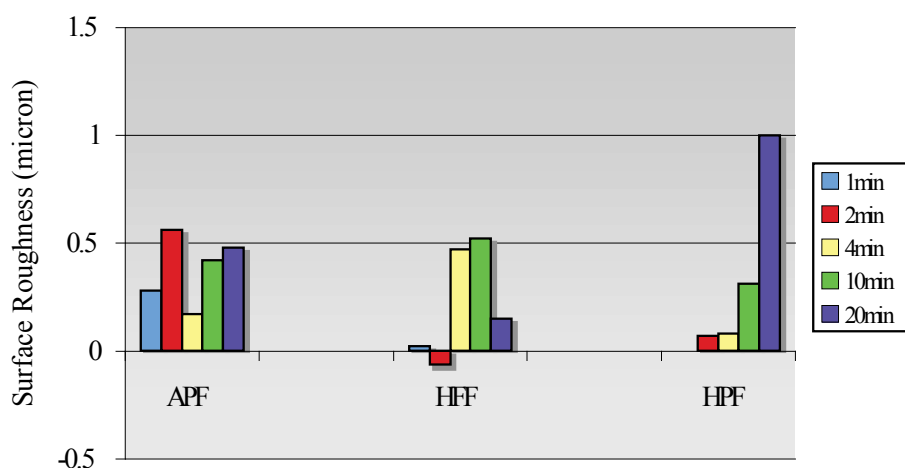


Figure 3: Etching effects of APF, HFF and HPF on Fuji IX as differences between exposure times and baseline control data for the same sample (Ra in μm).

The APF solution resulted in the greatest increase in roughness followed by the HFF solution and then the HPF solution. Figure 4 shows the mean increase in roughness above the background levels following exposure to solutions of tartaric acid, malic acid, maleic acid and PAA (all prepared with 2 g NaF) for up to 5 min. The results showed that the malic and maleic acid solutions have a greater etching effect than the APF solutions. The tartaric and PAA solutions caused much less etching but still matched the etching that resulted from APF.

The strength of the acid, as indicated by its ionic dissociation (K_a) in solution, contributes to its etching potential. Hydrofluoric acid (HF) has a K_a value of 6.46×10^{-4} and concentrated phosphoric acid (H_3PO_4) has a K_a of 7.1×10^{-3} , indicating that the latter is the stronger acid. However, HF has a particular affinity for reaction with calcium aluminium silicate and is used commercially as the most efficient glass etching chemical; therefore, the increased etching ability of HF might have been expected. However, hot concentrated ortho-phosphoric acid is also used commercially for glass etching. Of the alternative acids tested, L-tartaric acid has a K_a of 1.04×10^{-3} , and acrylic acid has a K_a of 5.6×10^{-5} .

However, in these reactions, each acid is mixed with a high concentration of NaF, and under strongly acidic conditions, extra HF will be formed, which would be expected to impact the acidic reaction.

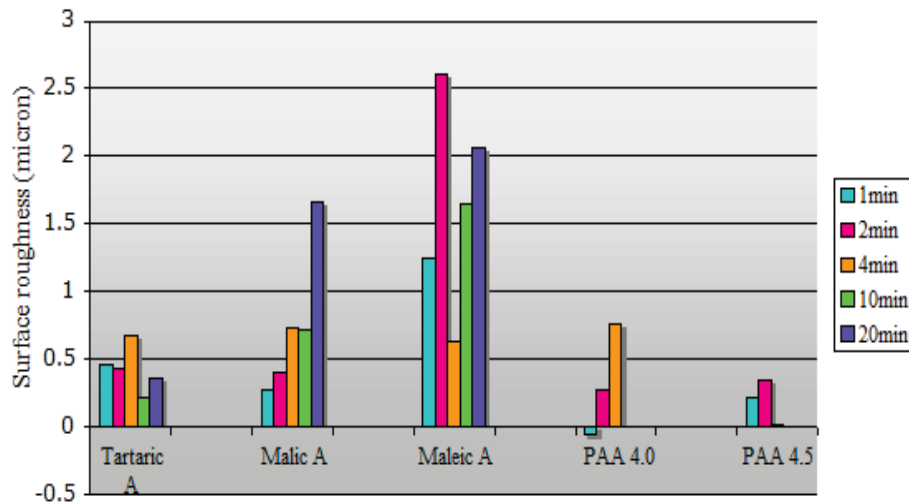


Figure 4: Etching effects of alternative acidulating systems as differences between exposure times and baseline control data for the same sample (Ra in μm).

The results using the APF solution showed an actual reduction in the Ra value of the traditional GICs within a minute of exposure to this solution. Later, the SEM assessment of change [Figure 2(a–e)] showed almost immediate substantial loss of the matrix followed by loss of filler particles, and thus this reduction in roughness was interpreted as resulting from the bulk surface loss of sufficient matrix and filler such that the surface was rendered smoother to the profilometer's stylus. For this reason, the time required for the initial surface roughness to appear was considered to be the most relevant parameter in determining the etching capabilities of the various acidic solutions.

This finding, in turn, might lead to questions regarding the exposure times selected for this study and whether they adequately simulated clinical exposures. Clinically, APF gels are applied professionally applied or self-applied by the patient, typically for four min periods. In cases involving high caries risk, daily application (self-applied for over 1 min) may be recommended and may continue over a prolonged time period. From the clinical experience of the authors, the initial visual etching of GICs and porcelain appears to have required daily use of this gel over a period of 6–12 weeks or weekly application over a year. It would be expected that the frequency of use and the salivary protection status of the patient, particularly the degree of buffering and oral clearance noted

within each patient's mouth, would greatly influence the degree of etching experienced. Therefore, the continued exposure for up to 20 min was designed to simulate the level of exposure experienced by a daily user with depleted salivary protection over a five-day period. The results, however, appear to simulate the level of exposure experienced clinically over a three-month period by such patients. This finding may point to the inadequacy of the *in vitro* tests in simulating the protective factors operating in the mouth, such as the layers of pellicle and plaque. However, it is not ethically feasible to conduct an *in vivo* analysis.

The high level of etching resulting from the alternative acids was surprising. Additionally, in retrospect, the choice of PAA was not wise, as this long-chain acid binds to calcium and has been shown to inhibit remineralisation when used as a saliva substitute in experiments conducted recently by Van de Reijden.¹²

4. CONCLUSION

Overall, these results suggested that a formula using only the phosphoric acid component for acidulation may be the only preferred alternative, with a reduction in application time of one or two minutes being necessary to avoid the acid's delayed etching effect.

5. ACKNOWLEDGEMENTS

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