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Laboratory Research

Effect of pH Variations in a Cycling Model on the Properties of Restorative Materials

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Clinical Relevance

When considering the individual needs of patients in the clinical setting, it is important to know the behavior of restorative materials in the oral environment under pH variations.

SUMMARY

This study evaluated the effect of cycling various pH demineralizing solutions on the surface hardness, fluoride release and surface properties of restorative materials (Ketac-Fil Plus, Vitremer, Fuji II LC, Freedom and Fluorofil). Thirty specimens of each material were made and the surface hardness measured. The specimens were randomized into five groups according to the pH (4.3; 4.6; 5.0; 5.5 and 6.2) of the demineralizing solution. The specimens were submitted to pH-cycling for 15 days. The specimens remained in the demineralizing solution for six hours and in the remineralizing solution for 18 hours. Then, the surface hardness (SH) was remeasured and the surface properties were assessed. Fluoride release was determined daily. Data from SH and the percentage of alteration in surface hardness were analyzed by analysis of variance ($p<0.05$); the Kruskal-Wallis test was performed for the fluoride release results. When hardness was compared, the variation in pH led to a positive correlation for glass ionomer cements and a negative correlation for fluoride release. For polyacid-modified resin composites, a negative correlation was found with regards to fluoride release; no significant correlation was observed for hardness. Surface properties were influenced: an acidic pH led to a greater alteration, except for polyacid-modified resin composites. The pH of the demineralizing solution influenced fluoride release from the tested materials. The pH variation altered hardness and surface properties of

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glass ionomer cements but did not influence polyacid-modified resin composites.

INTRODUCTION

The presence of fluoride in the oral environment influences cariogenesis, specifically at the tooth/restoration interface. Fluoride is of great importance for preventing initial demineralization and secondary caries at the restoration margins. Fluoride incorporated into restorative materials, as an inherent characteristic, may increase the longevity of restorative treatments, even when associated with other factors, including a patient's oral health care and his or her dentist's knowledge of the indication and performance of clinical procedures.

The chemical and physical characteristics and aspects related to the oral cavity may influence the properties of restorative materials.[1-2] Among these factors, the pH of dental biofilm undergoes variations during the demineralization and remineralization process *in vivo*, suggesting that the environment may influence the fluoride release of restorative materials, possibly due to changes in the physical and chemical structure of the materials.[3-4] In environments with high cariogenic challenges, changes in the surface characteristic of materials are present.[5] These changes influence the properties of surface hardness, which may also be influenced by the stage of the curing reaction and the composition of the restorative material.[3,6-8]

The methodology of the evaluation of restorative materials should simulate the situation in the oral cavity, especially with regard to alterations in the pH of dental plaque.[1,9-10] The pH-cycling mimics clinical conditions where there is always a dynamic between demineralization and remineralization.[10-11] Alterations in fluoride release by restorative materials may occur when the materials are compared using deionized water and pH-cycling.[10] However, the influence of pH variation on the performance of restorative materials is not well established.

This study evaluated the effect of demineralizing solutions with varying pH levels in pH-cycling on the surface hardness, fluoride release and surface characteristics of restorative materials.

METHODS AND MATERIALS

Experimental Design

For each material tested (Table 1), 30 specimens were fabricated, 5 mm in diameter and 2 mm thick, using a metallic template, following the manufacturer's instructions. Polymerization of the light cured materials was performed with a VIP unit (BISCO, Schaumburg, IL, USA) for 40 seconds at both sides of the specimen, using a light intensity of 500mW/cm^2. For the conventional material, pressure was applied for 10 minutes, until initial hardening. The specimens were submitted to the initial surface hardness (ISH) test one hour after they were made. During this period and for four additional hours, the specimens were stored in a covered plastic container and maintained in a humid environment. Thereafter, the specimens were submitted to pH-cycling and were immersed in demineralizing and remineralizing solutions for 15 days. Upon completion of each cycle and to aid in the assessment of fluoride release, the solutions were stored (-4°C) in polypropylene test tubes with lids. Upon completion of each period, the final surface hardness (FSH) was measured and analysis was performed using scanning electron microscopy. The variation factors adopted were the restorative materials and pH, and the variables employed to quantify the effect were the surface hardness, alteration in surface hardness (% ASH) and amount of fluoride release.

Experimental Groups and pH-cycling

Each material was divided into five experimental groups according to the pH level of demineralizing solution (De) used for pH-cycling as follows: 4.3; 4.6; 5.0; 5.5 and 6.2, with six specimens in each group. The specimens were randomly placed in polypropylene test tubes with lids. Inside the tubes, the specimens remained suspended using stainless steel wires. Each tube contained 2mL of the demineralizing or remineralizing (Re) solution.[11] Initially, the specimens were stored for six hours in De solution (2.0mmol L^{-1} Ca and P, in acetate buffer 75mmol L^{-1}). Then, the specimens were placed in new test tubes containing Re solution (Ca 1.5mmol L^{-1}, P 0.9mmol L^{-1}, KCl 150mmol L^{-1} in Tris buffer 20mmol L^{-1}, pH 7.0) for 18 hours.

The test tubes were subjected to constant shaking (shaking table TE-420 Orbital–Tecnal, Piracicaba, SP, Brazil) and were stored at 37±1°C. The specimens

Table 1: *Identification of the Materials Tested*

Material	Manufacturer	Classification	Batch #
Ketac-Fil Plus	3M/ESPE St Paul, MN, USA	Conventional glass ionomer cement	Liquid – 121077 Powder – 127039
Fuji II LC	GC Corporation Hasunuma-cho Itabashi-ku, Tokyo, Japan	Resin-modified glass ionomer cement	Liquid – 0205021 Powder – 0205091
Vitremer	3M/ESPE St Paul, MN, USA	Resin-modified glass ionomer cement	Liquid – 3BU Powder – 3GA
Freedom	SDI, Bayswater Victoria, Australia	Polyacid-modified resin composite	010368
Fluorofil (experimental)	BISCO, Schaumburg, IL, USA	Polyacid-modified resin composite	450-30-B

were rinsed with distilled/deionized water and dried with absorbent paper before being immersed in a new solution. The solutions were collected daily, identified and stored in polypropylene test tubes at -4°C to measure fluoride release.

Establishment of Surface Hardness–Initial and Final

Surface hardness was established with the aid of a microhardness tester meter (Shimadzu Micro Hardness Tester HMV-2000, Shimadzu Corporation, Kyoto, Japan) under a static load (Knoop) of 100 grams for five seconds. A total of five indentations were performed on the top surface of the material (ISH) at a 500 µm distance from each other. For FSH, five indentations were performed 250 µm from the initial indentations, and the percentage of alteration in surface hardness (% ASH) was calculated using the formula: [% ASH = ((FSH - ISH)/ ISH) x 100].

Establishment of Fluoride in the Solutions

Fluoride dosage was measured with a fluoride-specific electrode (Orion 9609-BN, Orion Research, Inc, Beverly, MA, USA) and a digital ion analyzer (Orion 720 A, Orion Research, Inc) previously calibrated with standard solutions (0.02 to 0.32 or 1 to 16 µg F/mL), according to the fluoride concentration in the samples expressed in µg F/cm^2. Before reading, TISAB III (Thermo Orion, Beverly, MA, USA) was added at a ratio of 1:10, and the fluoride was dosed while the solution was being constantly shaken (TE-081–Tecnal, Piracicaba, SP, Brazil). The fluoride concentrations of the solutions were separately established. Then, the results of the De and Re solutions were added (De+Re), finalizing a 24-hour period and one cycle of the methodology completed (pH-cycling).

Scanning Electron Microscopy

For each experimental group, four specimens that had been submitted to pH-cycling were randomly selected for SEM analysis. Additional specimens of the materials (n=4) were made to compare the baseline surface characteristics with those of the tested groups. The specimens were sputter coated in a SCD 050 machine (BAL-TEC S/A, Balzers, Liechtenstein) for deposition of a 20-nm layer of gold. After this procedure, the specimens were analyzed at 2,000x magnification with a scanning electron microscope (Digital Scanning Microscope DSM-960, Zeiss, Munich, Germany). The qualities of the surfaces examined were subjectively assessed, with details of the surfaces being recorded as observations.

RESULTS

The normality test was applied to the data of ISH, FSH and % ASH. After confirmation of homogeneity, the results were assessed by analysis of variance and the Tukey test. The fluoride release results were heterogeneous and, thus, were submitted to the Kruskal-Wallis test. The data of fluoride release and % ASH were also submitted to Pearson correlation. Analyses were performed with GMC version 2002 software[12] at the 5% significance level.

Table 2 displays the hardness results according to the variation in pH of the demineralizing solution for each material tested. There was a statistical difference between ISH and FSH of the restorative materials for all pH values. Ketac-Fil Plus and Fluorofil displayed the highest initial surface hardness ($p>0.05$), whereas, Freedom revealed the lowest value ($p<0.05$). The lowest values of FSH were found at the lowest pH, except for Freedom and Fluorofil, which presented no differences in FSH with the pH variation ($p>0.05$).

Table 3 presents the alteration of surface hardness (% ASH) results according to the pH variation of the dem-

Table 2: *Values (mean (sd), n=6) of Initial (ISH) and Final (FSH) Surface Hardness for pH x Restorative Material*

pH	**FSH**				
	Ketac-Fil Plus	Fuji II LC	Vitremer	Freedom	Fluorofil
ISH	^{e}65.0 (2.7)^{A}	^{c}38.2 (2.5)^{B}	^{c}49.5 (1.2)^{C}	^{b}24.2 (1.7)^{D}	^{b}65.0 (1.0)^{A}
4.3	^{a}55.4 (2.3)^{A}	^{a}45.3 (2.3)^{B}	^{a}36.4 (3.2)^{C}	^{a}29.4 (2.4)^{D}	^{a}43.8 (2.5)^{B}
4.6	^{b}73.4 (2.7)^{A}	^{a,b}48.3 (3.1)^{B}	^{a}40.2 (1.5)^{C}	^{a}30.6 (2.4)^{D}	^{a}44.3 (1.8)^{B}
5.0	^{b}77.7 (4.1)^{A}	^{b}50.7 (1.6)^{B}	^{b}46.3 (0.5)^{B}	^{a}31.4 (2.7)^{C}	^{a}43.4 (1.4)^{B}
5.5	^{c}85.4 (1.5)^{A}	^{b}50.7 (3.7)^{B}	^{b}50.6 (0.3)^{B}	^{a}30.2 (2.7)^{C}	^{a}41.3 (0.7)^{D}
6.2	^{d}91.6 (4.6)^{A}	^{b}51.9 (1.9)^{B}	^{b}48.3 (1.1)^{B}	^{a}30.5 (1.1)^{C}	^{a}41.6 (1.3)^{D}

Means followed by different letters are statistically different (5%). Lower case letters demonstrate comparison within each material. Capital letters indicate comparison of surface hardness between materials.

Table 3: *Values (mean (sd), n=6) of % ASH for pH x Restorative Material*

pH	**% ASH**				
	Ketac-Fil Plus	Fuji II LC	Vitremer	Freedom	Fluorofil
4.3	^{a}-15.0 (3.8)^{A}	^{a}19.1 (3.2)^{B}	^{a}-27.0 (4.9)^{C}	^{a}22.0 (2.0)^{B}	^{a}-33.2 (2.8)^{C}
4.6	^{b}12.4 (2.5)^{A}	^{a}23.0 (4.7)^{B}	^{a}-18.4 (2.7)^{C}	^{a}26.1 (2.6)^{B}	^{a}-32.2 (3.0)^{D}
5.0	^{b}20.4 (3.8)^{A}	^{b}33.7 (6.3)^{B}	^{b}-6.7 (1.7)^{C}	^{a}29.5 (3.6)^{B}	^{a}-34.0 (1.6)^{D}
5.5	^{c}33.1 (3.5)^{A}	^{b}33.0 (4.6)^{A}	^{b}2.0 (0.7)^{B}	^{a}25.0 (5.8)^{A}	^{a}-36.8 (1.0)^{C}
6.2	^{c}39.9 (5.4)^{A}	^{b}36.1 (9.4)^{A}	^{b}-2.0 (1.8)^{B}	^{a}26.9 (5.6)^{C}	^{a}-36.3 (1.8)^{D}

Means followed by different letters are statistically different (5%). Lower case letters demonstrate comparison within each material and capital letters indicate comparison between materials.

Table 4: *Values (mean (sd), n=6) of Fluoride Concentration (µg F/cm^2) for Restorative Material x pH*

pH	Materials				
	Ketac-Fil Plus	Fuji II LC	Vitremer	Freedom	Fluorofil
4.3	^{a}8.8 (8.8)^{A,B,D}	^{a}7.6 (7.0)^{B,D}	^{a}10.5 (9.6)^{A}	^{a}2.7 (2.1)^{C}	^{a}6.0 (4.3)^{D}
4.6	^{b}5.4 (6.3)^{A}	^{a}5.7 (4.7)^{A,B}	^{a}7.4 (7.1)^{B}	^{a}2.1 (1.7)^{C}	^{b}3.0 (3.4)^{C}
5.0	^{c}3.5 (4.4)^{A,C}	^{b}3.6 (2.7)^{A,B}	^{b}4.6 (4.6)^{B}	^{a,b}1.9 (1.5)^{C}	^{c}1.0 (1.3)^{D}
5.5	^{d}1.9 (2.4)^{A}	^{c}2.5 (1.8)^{B}	^{c}2.9 (2.7)^{B}	^{b}1.5 (1.4)^{A}	^{d}0.6 (0.4)^{C}
6.2	^{d}1.7 (2.4)^{A}	^{c}2.2 (1.6)^{B}	^{c}2.2 (2.0)^{B}	^{b}1.2 (1.4)^{A}	^{d}0.6 (0.3)^{C}

Means followed by different letters are statistically different (5%). Lower case letters demonstrate comparison within each material and capital letters indicate comparison between materials.

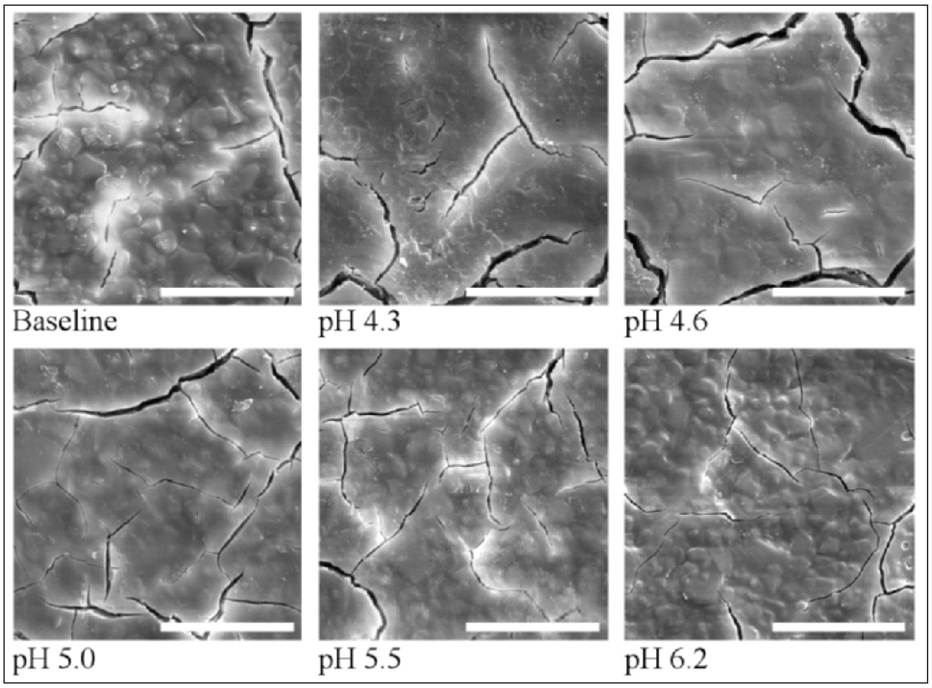

Figure 1. *Baseline and post-cycling photomicrographs of Ketac-Fil Plus in accordance with the variation in pH of the demineralizing solution. 2,000x magnification. Bar 20 µm.*

ineralizing solution for each material tested. In the polyacid-modified resin composites, the % ASH was not influenced by the variation in pH (p>0.05); however, the % ASH increased for Freedom, while for Fluorofil, it diminished. The resin-modified and conventional glass ionomers revealed a variation in the % ASH values, with the change in pH. Among the resin-modified cements, Fuji II LC presented an increase in % ASH compared with Vitremer (p<0.05). A positive correlation was found for the pH and % ASH interaction and was statistically significant for Ketac-Fil Plus (r=0.98; p=0.01), Fuji II LC (r=0.97; p=0.03) and Vitremer (r=0.99; p=0.000001) but was not significant for Freedom (r=0.41; p=0.50) and Fluorofil (r=-0.86; p=0.41).

Table 4 shows the outcomes of fluoride release of the restorative materials for the interaction between the material and pH according to the variation in pH of the demineralizing solution. The materials investigated presented the highest values of fluoride release at pH levels 4.3 and 4.6. At these levels of pH, Vitremer revealed the highest fluoride release, followed by Ketac-Fil Plus and Fuji II LC, Fluorofil and Freedom. At pH levels 5.5 and 6.2, Vitremer and Fuji II LC exhibited similar results (p>0.05), as well as Ketac-Fil Plus and Freedom (p>0.05). The pH and fluoride release interaction presented a negative correlation for all materials (Ketac-Fil Plus r=-0.97, p=0.01; Fuji II LC r=-0.99, p=0.000001; Vitremer r=-0.99, p=0.000001; Freedom r=-0.96, p=0.04; Fluorofil r=-0.98, p=0.005).

When the correlation between surface hardness and fluoride release was verified, a negative correlation was found for Ketac-Fil Plus (r=-0.99; p=0.000001), Fuji II LC (r=-0.97; p=0.0098) and Vitremer (r=-0.98; p=0.0022). Freedom (r=-0.54; p=0.50) and Fluorofil (r=-0.69; p=0.48) showed no statistically significant correlation.

Figures 1 through 5 present SEM photomicrographs of the surfaces of the materials investigated. Ketac-Fil Plus, Fuji II LC and Vitremer were influenced by the variation in pH of the demineralizing solution as to their surface characteristics being more evident at lower pH levels. This was not observed for the polyacid-modified resin composites Freedom and Fluorofil.

DISCUSSION

In the assessment of restorative materials, surface hardness is an important physical characteristic for the comparative study of dental materials, and it is a valuable parameter with regards to the assessment of interaction between the material surface and medium in which it is found.[13] This interaction may be better presented when the surface conditions are observed with scanning electronic microscopy, a widely used method.[14-16] This methodology may, however, submit the specimens to adverse conditions inside the equipment as they become dehydrated, resulting in small cracks and fractures.[16] This aspect can be minimized when the evaluation is carried out on a larger surface and in more than one specimen.[17]

There are several factors that contribute to an acidogenic environment within the oral cavity due to cariogenic microorganisms or acidic food, ionic composition and ionic strength of saliva or enzymatic attacks. Bacteria and products are responsible for the majority of acid production, which occurs shortly after exposure to dietary carbohydrates. In this study, several conditions common to the oral environment were not considered in order to highlight the focus of the analysis, which was the physicochemical factors related to the onset and development of carious lesions. Taken together with the findings of similar investigations, the outcomes of this study are important for predicting the clinical performance of these materials.

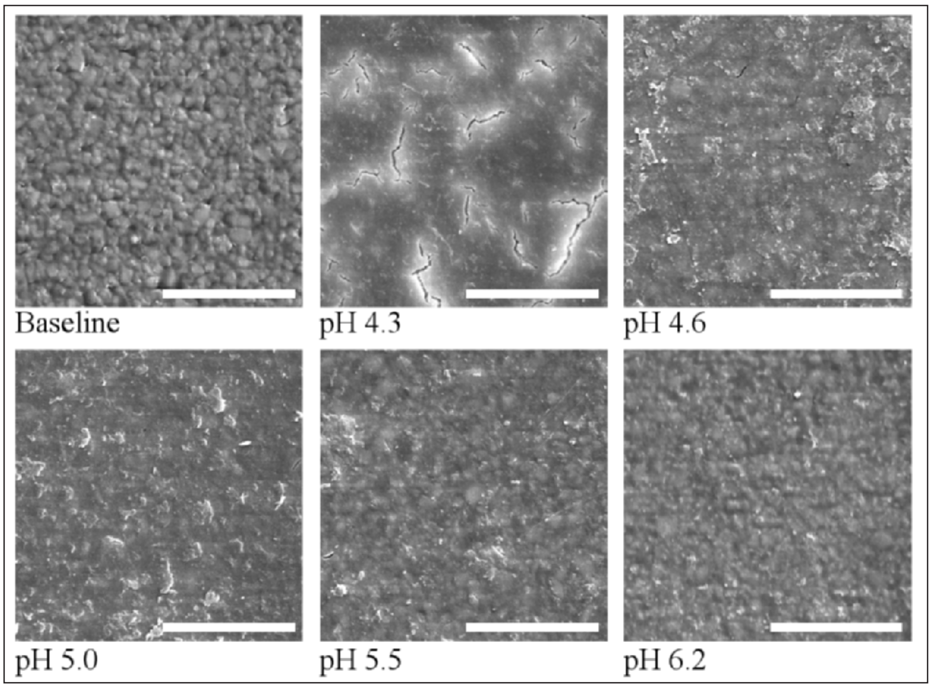

Figure 2. *Baseline and post-cycling photomicrographs of Fuji II LC in accordance with the variation in pH of the demineralizing solution. 2,000x magnification. Bar 20 μm.*

Considering that the critical pH of enamel is different from that of dentin, this methodology comprised a pH variation ranging from 4.3 to 6.2 in the demineralizing solution. Saliva may protect enamel at a pH higher than 5.5 and dentin at a pH higher than 6.5.[18] However, the critical pH is not the same in the presence of fluoride. Thus, fluoride-releasing restorative materials may contribute to the balance in critical oral pH[19] by reducing the demineralization periods and making the remineralization cycles more frequent and longer.

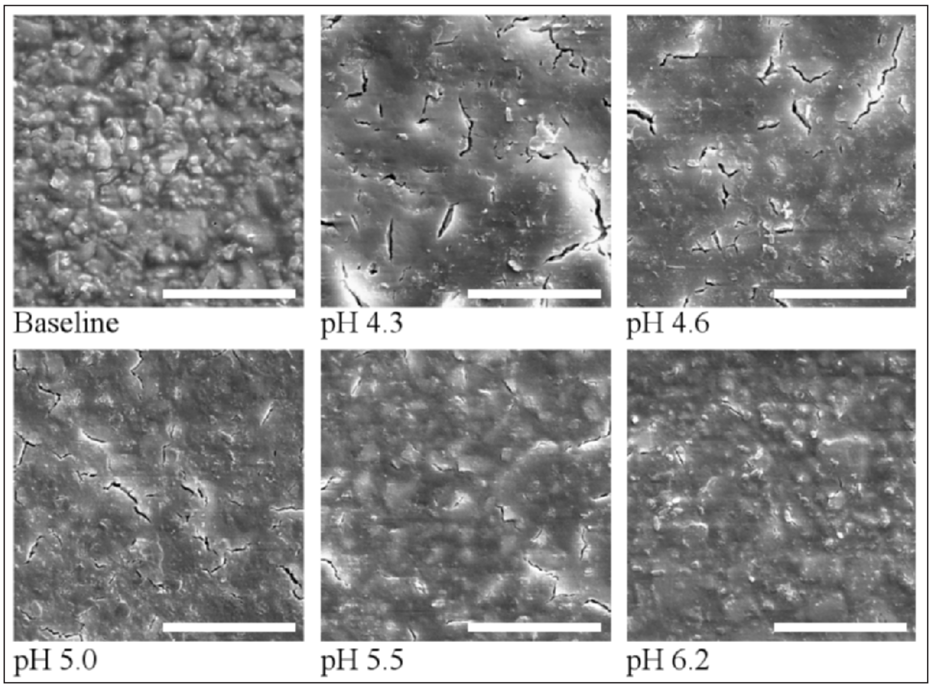

Figure 3. *Baseline and post-cycling photomicrographs of Vitremer in accordance with the variation in pH of the demineralizing solution. 2,000x magnification. Bar 20 μm.*

The pH variation that occurs in dental biofilm may change the investigated properties of restorative materials. The change in surface hardness was found to be related to the pH of the environment for glass ionomer cements (Ketac-Fil Plus, Fuji II LC and Vitremer) with a positive correlation. The immersion of resin-modified glass ionomer cements in aqueous solutions may increase or reduce their hardness, depending on several factors, including the time and means of immersion and the composition of the material.[3] Thus, the amount of resin matrix (HEMA) in the cement influences the water absorbed by these materials.[20] The absorbed water may inhibit the secondary curing reaction at the superficial layer of the cement, reducing its hardness.[21] These factors may also explain the outcomes achieved with polyacid-modified resins, since the hardness (Table 2) and surface characteristics (Figures 4 and 5) were not influenced by the pH, yet they presented variations in % ASH (Table 3). Because Ketac-Fil Plus is a conventional material, it should have been more influenced by the aforementioned factors; however, it presented an increase in % ASH, except when exposed to pH 4.3, possibly due to the size and shape of the fillers[8] and the continued curing reaction process.[6-7]

Polyacid-modified resin composites presented a lower rate of fluoride release compared to resin-modified and conventional glass ionomer cements (Table 4), as was also observed in previous studies.[10,22-23] This difference in results may probably be related to the composition,[24] solubility,[25] diffusion of fluoride ions,[19,26] porosity and powder:liquid ratio.[24]

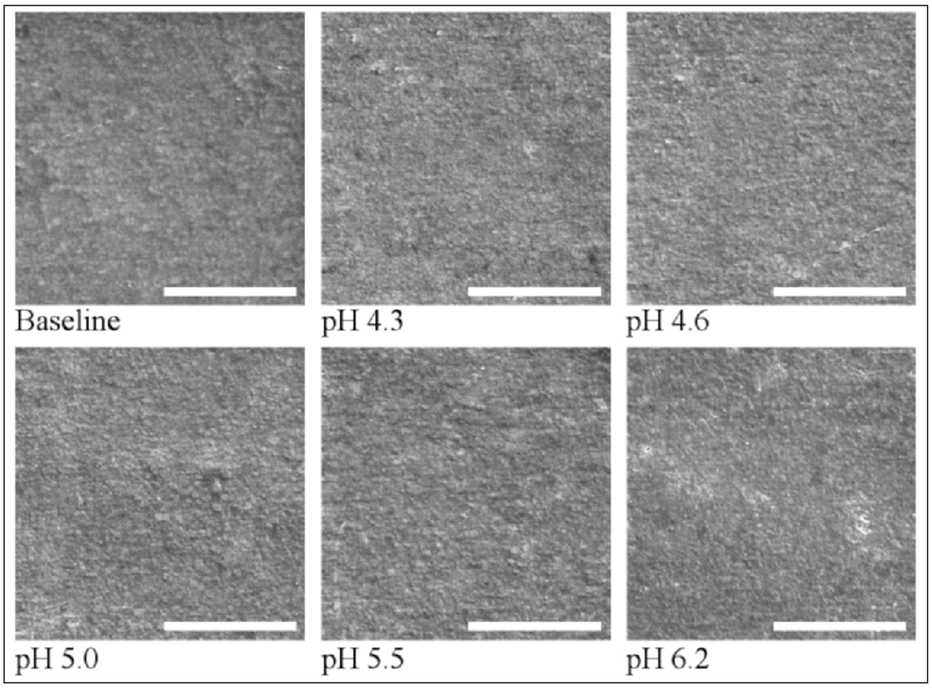

Figure 4. *Baseline and post-cycling photomicrographs of Freedom in accordance with the variation in pH of the demineralizing solution. 2,000x magnification. Bar 20 µm.*

Fluoride release seems to be pH-dependent; a greater amount of fluoride is released by restorative materials when the solution has a low pH (Table 4), thus presenting a negative correlation. Published data[1,10,27] shows a higher release in an acidic environment compared to a neutral environment, yet, with no changes in pH. This high fluoride release suggests an increase in dissolution of the material and may be observed on the surface characteristics (Figures 1, 2 and 3) and hardness values (Tables 2 and 3). This may be confirmed, as a statistically significant correlation is observed between hardness and fluoride release for most of the materials (Ketac-Fil Plus, Fuji II LC and Vitremer). Dissolution of the material was not observed for the polyacid-modified resin composites (Figures 4 and 5). This fact may have contributed to the lower fluoride release of these materials when compared to the other cements. The minimum concentration of fluoride that would provide a better effect in reducing the progression of carious lesions is not known. Due to the multifactorial nature of caries, each individual may require a different fluoride concentration, depending on the risk or caries activity of the patient. Therefore, in these groups of patients, the utilization of dental materials with fluoride release in the long-term should be preferred.[28]

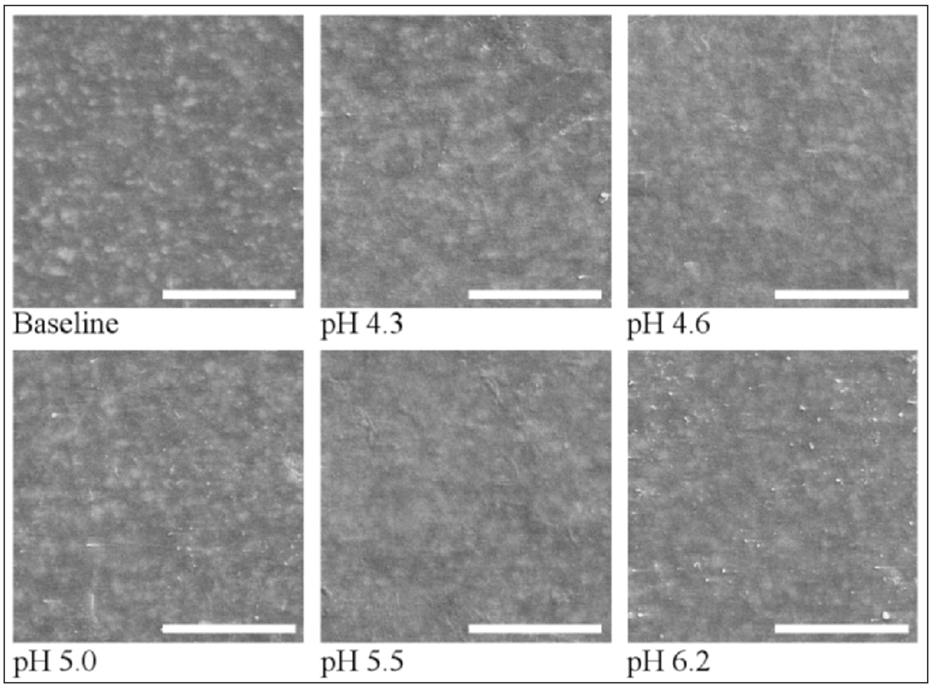

Figure 5. *Baseline and post-cycling photomicrographs of Fluorofil in accordance with the variation in pH of the demineralizing solution. 2,000x magnification. Bar 20 µm.*

The results of this study demonstrated that the properties of restorative materials were influenced by pH variation, highlighting the importance of accomplishing *in vitro* experiments that simulate the cariogenic challenge with characteristics comparable to those observed *in vivo*.

The indication of a restorative material has greater clinical impact when associated with patient commitment to oral hygiene and a low-sugar diet, because non-compliance with these factors is directly related to long, frequent periods of low pH in the mouth. Thus, it is clinically relevant to understand the performance of materials in situations with pH variations in the environment, since they should be able to provide the best clinical performance in situations of both high and low cariogenic challenge for maintenance of the patient's oral health.

CONCLUSIONS

The variation in pH of the demineralizing solution for pH-cycling influenced fluoride release of the materials tested. This variation altered the hardness and surface characteristics of glass ionomer cements, yet, it did not induce such changes in polyacid-modified resin composites.

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