Abstract: This *in vitro* study was performed to evaluate the surface roughness (Ra) and morphology by scanning electron microscopy (SEM) of composite resins that had been stored in acidic solutions typical of those present in the diet. Three composite resins (4 Seasons, Z250, and P90) were selected and divided into three groups (*n* = 7) according to the solutions tested: G1: distilled water; G2: Coca-cola, and G3: orange juice. The *Ra* test was repeated after immersion periods of 15, 90, and 180 days. The mean *Ra* values were subjected to LS means analysis and the Tukey-Kramer (*P* < 0.05). One test specimen of each composite resin was selected for SEM analysis after each period. The *Ra* data indicated that P90 had the lowest *Ra* values. 4 Seasons and Z250 had statistically similar roughness values for all the solutions and evaluation periods. With the exception of 180-day immersion in Coca-cola, 4 Seasons showed significantly higher values than Z250. SEM analysis showed that P90 was the composite resin most resistant to the actions of all acid solutions for the periods analyzed. Interaction between components of the solutions and the active components of other dietary items, as well as oral hygiene, may affect the chemical degradation of composite resins.

Keywords: acids, composite resins, degradation, roughness, scanning electron microscopy

Introduction

The use of composite resins in anterior and posterior teeth has increased substantially over the last few years because of their esthetic characteristics [1]. These materials have been modified and improved in a manner not previously seen in any other type of restorative material, making them one of the greatest successes in dentistry [2].

Composite resins are usually composed of an organic matrix and filler particles [3]. In the organic matrix, the monomeric combination used most frequently is that of bisphenol A glycol dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA). The presence of the OH groups in the Bis-GMA molecule is responsible for the water absorption and solubility characteristics of composite resins. Water absorption by the hydroxyl groups leads to plasticization of the polymer and consequent degradation of the chemical and mechanical properties, in addition to staining susceptibility [4-6]. Therefore, substitution of the pendant hydroxyl groups (OH-) by methyl groups (CH3 Bis-GMA), producing a molecule (Bis-EMA) that has a higher molecular weight and lower viscosity than the Bis-GMA monomer, has been suggested. This results in formation of a composite resin with lower solvent degradation, reduced water absorption, lower polymerization shrinkage and greater clinical durability [3,7].

Despite recent technological advances in the composition of methacrylate-based composite resins, stress due to volumetric shrinkage of the dimethacrylate monomers during light-activated polymer conversion continues to be a problem [8]. This situation results in reduced marginal integrity and possible postoperative problems [9]. These challenges have led to the development of a system based on the association of siloxane and oxirane monomers, denominated "silorane". Silanized quartz particles with a mean size of 0.47 µm comprising 58% by volume of the composition confers physical properties similar to those of dimethacrylate-based composite resins [10].

Incorporation of filler particles into the organic matrix of composite resins leads to an improvement of physical and mechanical properties. These particles may be of quartz, colloidal silicon, barium, strontium or lithium glass [11-13]. Thus, whatever the content of the composite resin, the resulting physical properties and degree of conversion must guarantee that the restorative material is resistant to the action of solvents in the oral medium. In this connection, the pH of the oral medium and the period of contact with the solution have a considerable influence on the onset of degradation of the restoration surface. Acid solutions cause erosion of the agent coating the filler particles of the composite resin, causing loss of hardness due to hydrolysis at the interface where the dimethacrylate bonds to the organic matrix [7]. The aim of the present study, therefore, was to evaluate the surface roughness of composite resins with different organic matrices after storage in acidic solutions typical of those consumed in the diet for periods of up to 180 days. The null hypothesis was that acidic beverages would not affect the susceptibility of composite resins with different organic matrices to alterations in surface roughness.

Materials and Methods

Three composite resins widely employed for restoring anterior and posterior teeth were selected for this study. The first type comprises micrometer-order inorganic particles (size range 0.4-0.6 µm) 4 Seasons (Ivoclar Vivadent, Schaan, Liechtenstein). The second type has a Bis-EMA-based organic matrix and 0.4-µm inorganic particles Z250 (3M Oral Care, St. Paul, MN, USA). The third type P90 (3M Oral Care) with a siloxane/oxirane-based organic matrix, also contains micrometer-order inorganic particles (0.47 µm). Technical details of these composite resins, including their basic composition, manufacturer and lot number, are shown in Table 1.

Test specimen preparation

A polynvinyl siloxane matrix 4 mm in diameter and 2 mm thick was used to make the test specimens. The composite resins were inserted into the matrix in two increments. A 10-cm length of dental floss was interposed between the composite resin increments, thus allowing the test specimens to be suspended in the solutions. A polyester strip (Probem Ltda, Catanduva, Brazil) was then placed over the composite resin and finger pressure was applied with the aid of a 2-mm thick glass plate. The material was light-activated for 40 s through the polyester strip using an Elipar FreeLight 2 LED (3M Oral Care) light unit with a power density of 1,200 mW/cm², gauged on a radiometer (L.E.D Radiometer, Kerr, CA, USA), with an emitted light wavelength of 440-490 nm. One test specimen was randomly separated for scanning electron microscopy (SEM) evaluation after each storage period (*n* = 7).

After polymerization, the test specimens were stored in distilled water at 37°C for 24 h [14]. They were then subjected to surface polishing (top surface) with fine and superfine-grain aluminum oxide discs (Soft Lex Pop On/3M Oral Care) mounted in a low-speed handpiece (KaVo, Biberach
an der Riss, Germany). Between one disc and the next, the test specimens were cleaned with jets of air/water and in water under ultrasound for 15 min. On conclusion of polishing, the test specimens were again cleaned in distilled water in an ultrasound bath (Ultrasonic Cleaner, USC1400, Unique Ind Ltda, São Paulo, Brazil) for 30 min to remove any polishing debris. During the ultrasound bath cleaning, the distilled water was changed every 10 min.

**Surface roughness**

The surface of each test specimen was carefully dried with absorbent paper to allow measurement of surface roughness. For this purpose, three readouts of the real profiles of the surface of each test specimen were taken, and the arithmetic mean of the readouts was taken as the representative value.

The analysis of the surface roughness was performed by a Rugsometer (Surfcorder SE 1700, Tokyo, Japan) equipped with a diamond stylus 2 µm in diameter of maximum ranges 125 μm in the horizontal and vertical directions (x and y axes). The parameter Ra (mean roughness) was used, which represents the value of the arithmetic mean of all the absolute distances of the roughness profile (R) starting from the central line, within the mean extension Lm (Limit of measurement = the extension considered in readouts, including the standard deviation in the respective experimental groups, are presented in Table 3). The mean values obtained during the test specimen surface roughness readouts, including the standard deviation in the respective experimental groups, are presented in Table 3.

**Results**

For this analysis, the selected specimens were ultrasonically cleaned (Ultrasonic Cleaner, USC1400, Unique Ind Ltda) for 30 min, the water being changed every 10 min. The samples were mounted on metal stubs and left overnight in a silica gel desiccator. They were then mounted in a sample carrier and sputter-coated with gold-palladium under high vacuum (Balzer-SCD 050 Sputter Coater, Balzers Union Aktiengesellschaft, Tritzen, Liechtenstein). SEM examination was conducted using a spot size of 5.8 -15 kV with a 10-mm WD.

**Statistical analysis**

Initially, descriptive and exploratory data analyses were performed. This involved graphical analyses of the data and standardized residues, as well as application of the Shapiro-Wilk test to verify the normality of errors. As the same specimens were used for measurement of surface roughness for all evaluated periods, mixed models were used for repeated measures over time (Proc Mixed procedure) employing the SAS statistical software package (SAS Institute North Carolina State University). The design model was considered to involve graphical analyses of the data and standardized residues, as well as application of the Shapiro-Wilk test to verify the normality of errors.

### Table 1 Description of composite resins used in the study

| Material      | *Composition | Particle size (µm) | Manufacturer     | Shade | Lot     |
|---------------|--------------|--------------------|------------------|-------|---------|
| 4 Seasons     | Bis-GMA, TEGDMA, UDMA | 0.4 to 3           | Ivoclar vivadent | A3    | J16883  |
| Filtek Z250   | Bis-GMA, Bis-EMA and UDMA, Particles: silicon/zirconium (60% by volume), photoinitiator | 0.6 | 3M Oral Care | A3    | 7WM     |
| Filtek P90    | Siloranes, Particles: quartz | 0.47 | 3M Oral Care | A3    | 8AP     |

*Information was provided by the manufacturers Bis-GMA, bisphenol-A dimethacrylate glycidyl, UDMA, urethane dimethacrylate, Bis-EMA, bisphenol A ethoxylate dimethacrylate, TEGDMA, triethylene glycol dimethacrylate.*

### Table 2 Description of the solutions used, showing pH values

| Solutions     | pH | Composition                                                                 | Brand name                  |
|---------------|----|----------------------------------------------------------------------------|------------------------------|
| Distilled water | 7.0 | Distilled water                                                             |                              |
| Coca-cola classic | 2.73 | Carbonated water: 2,400 g, sufficient water to dissolve caramel: 37 g, caffeine: 3.1 g, phosphoric acid: 11 g, decaffeinated cola extract: 1.1 g, cola nut: 0.37 g | Coca-cola classic/Coca-cola LTDA |
| Orange juice  | 3.58 | Water, sugar, concentrated orange juice, acidulants: citric acid, aromatizing agent: natural orange aroma, vitamins A and D, stabilizers: agar gum and natural coloring agents: curcuma and urucum. Does not contain gluten. | Purity/Cocamar               |

### SEM evaluation

One test specimen of each composite resin that had been immersed in each solution was selected after periods of 24 h, and 15, 90, and 180 days, and examined with a scanning electron microscope (JEOL- JSM 5600, Tokyo, Japan) at ×3,000 magnification to verify any alterations in microstructure.
of the materials varied depending on the materials and the storage time. Thus, the effect of test solutions on the Ra equivalent to 720 h of exposure. In the present study, composite resins equal to 10 h per month. Direct contact for 24 h for 30 days would be the consumption of 2 L of water divided into 8 glasses (250 mL each) were made according to the protocol of Von Fraunhofer [18]. Based on certain solutions on composite resin restorations, some projections of previous studies [15-17]. In order to evaluate the clinical effect of exposure evaluated solutions for up to 180 days, thus corroborating data from previous studies. The results of the present study revealed morphological alterations in the surface of different composite resins after exposure to various acidic substances typical of those ingested in the daily diet for a period of six months, thus rejecting the null hypothesis.

All of the composite resins evaluated showed a significant gradual increase in the surface roughness value after immersion in all of the evaluated solutions for up to 180 days, thus corroborating data from previous studies [15-17]. In order to evaluate the clinical effect of exposure to certain solutions on composite resin restorations, some projections were made according to the protocol of Von Fraunhofer [18]. Based on the consumption of 2 L of water divided into 8 glasses (250 mL each) per day and a resident time in the mouth of 20 s, the exposure would be equal to 10 h per month. Direct contact for 24 h for 30 days would be equivalent to 720 h of exposure. In the present study, composite resins were exposed to storage solutions for periods of up to 180 days, equivalent to daily consumption for approximately three years, which is a reasonable period for evaluating the chemical degradation of composite resin restorations present in the oral cavity. Thus, the effect of test solutions on the Ra of the materials varied depending on the materials and the storage time [19]. For instance, the highest Ra values for Z250 and 4 Seasons were shown for acidic solutions. Because roughness is a surface property, it is affected by water sorption, which is a complex phenomenon dependent on the matrix resin, filler, and interfacial bonding between the particles and the matrix [19,20]. Decreased filler loading has been shown to result in greater water absorption. Other parameters, such as differences in shape, hardness, distribution, and amount of particles, could also contribute to the Ra of materials [21,22].

4 Seasons and Z250 showed gradual and statistically significant increases in surface roughness values for up to 90 days in all the solutions evaluated. These results corroborate a previous study showing that all storage solutions produced rougher surfaces on the specimens [21]. For methacrylate composites, Hawang et al. [22] also found that storage time had more influence on the increase in surface roughness than the type of acidic solution.

In addition, 4 Seasons continued to undergo a significant increase in surface roughness for up to 180 days. In P90, a significant increase in roughness occurred between the initial period and 30 days for all the evaluated solutions. This result appears to corroborate the study by Soderholm [23], who showed that there was greater difficulty in the silanization process of barium-based filler particles (as is the case with 4 Seasons), with the result that these could be more easily dislodged when immersed in water or acid solutions, in comparison with filler particles composed of quartz (P90), and zirconia/silica (Z250), as shown in the present SEM photographs (Fig. 1). This condition resulted in a higher roughness value and alteration of the surface morphology, which increased with storage time because this favored hydrolytic degradation. On the other hand, the surfaces of filler particles such as zirconia/silica (Z250) and quartz (P90) are more reactive in the covering process promoted by silane and this favors the bond, thus consequently facilitating greater resistance to hydrolytic degradation in an acid medium [24].

Hydrolytic degradation can be explained by the autocatalytic reaction of water with the filler particle coating agent (R-Si-O-Si-R), which forms a pendant silanol (SiOH) radical during the chemical bonding reaction. This allows the filler particle to bond to the organic matrix of the composite resin. According to the catalytic reaction, the natural polarity of water is capable of breaking the bond (R-Si-O-Si-R) through binding of the oxygen atom of water with silicon. The moment this bond occurs, the silicon is displaced, causing ionic hydrolysis and hydrolytic degradation of the filler particle surfaces. This degradation depends on the quality of the filler particle bond to the coating agent (silane), as explained by Yoshida et al. [25].

Chemical degradation also acts on the organic matrix of composite resins due to the natural heterogeneity of the polymerization process of methacrylate-based monomers [26]. During polymerization, the multifunctional monomers form regions of microgels and micropores located among the cross-links close to the pendant terminals of the double carbon bonds. The unreacted monomers are located in these regions, forming an agglomerate of residual monomers [27]. When water penetrates into the organic matrix and expands the spaces among the polymer cross-links, it causes changes in the mass and dimensions of the polymer. The residual monomers are solubilized by the solvent solution and may be displaced...
from the polymer mass. Thus, the processes of both expansion and leaching occur through the diffusion of water into the polymer. It has been reported that monomers trapped in the region of micropores are more susceptible to leaching than those retained in the microgels. Thus, the displacement of monomers may be affected by not only the quantity of residual monomers, but also the distribution of monomers inside the polymer formed [3]. This may explain the results of the present study, in which P90 showed significantly the lowest surface roughness for all the solutions and periods evaluated. In P90 the polymerization reaction is based on the opening of the cationic rings of the oxirane radicals; any residual monomers are practically non-existent, making it more resistant to hydrolytic degradation [7, 10, 28]. In addition, incorporation of the silorane molecule resulted in a material with greater hydrolytic stability, in comparison with composite resins based on methacrylate monomers [29].

4 Seasons and Z250 showed statistically similar roughness values for all of the solutions and evaluation periods. With the exception of immersion in Coca-cola (pH 2.73) for 180 days, 4 Seasons showed significantly higher values than Z250. According to Miranda [30], pH is the most relevant factor determining the erosive potential of a solution. Furthermore, Shabanian et al. [24] reported that the lower the pH of a solution, the greater it will damage the mechanical performance of composite resins. Jensdotir et al. [31] observed that the erosive potential of some beverages in the first minutes of exposure was solely dependent on pH, and that Coca-cola “Classic” is approximately ten times more erosive than orange juice. As 4 Seasons is composed of the monomers Bis-GMA, TEGDMA and UDMA, this makes it more susceptible to the action of Coca-cola in comparison with Z250, which is composed of more resistant monomers ( Bis-EMA, Bis-GMA and UDMA) [3]. In addition, 4 Seasons has irregularly shaped load particles, which may contribute to the increase in roughness observed after immersion in all solutions tested [32]. Morphological analysis revealed that after chemical degradation, the load particles were displaced, leaving empty spaces that made the resin surface more porous, as observed for 4 Seasons, whereas Z250 and P90 showed a more cohesive and uniform surface, despite small ruptures in the continuity of the organic matrix (Fig. 1).

The greatest increase in surface roughness values was observed for 4 Seasons immersed in Coca-cola for 180 days. Among the materials, P90 showed the best results in terms of both surface roughness and surface morphology for the different solutions and periods evaluated. This indicates that surface roughness and chemical degradation are dependent on resin composition, as observed by Yazici et al. [33]. Thus, the composite resin with more hydrophobic monomers (P90) was more resistant to chemical degradation and surface roughening than the conventional composite resins for all the solutions and periods of time evaluated. Clinically, however, the effects of acid solutions on composite resins may differ. In the oral cavity, parameters such as changes in pH, salivary enzymes, the ionic composition of foods, beverages or saliva—as well as oral hygiene—may operate alone or in combination with mechanical factors such as abrasion and/or fatigue, thus affecting the process of chemical degradation and the surface roughness of composite resins.

Conflict of interest
None.

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