Effects of mouthwashes on Knoop hardness and surface roughness of dental composites after different immersion times

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Abstract: The aim of this *in vitro* study was to evaluate the effect of different mouthwashes on superficial roughness and Knoop hardness of two resin composites. Eighty specimens (6 mm ∅ and 2 mm height) were prepared and divided into eight experimental groups (n = 10) according to the resin composites (4 Seasons and Esthet X), and storage solutions (G1 - Distilled water; G2 - Colgate Plax Overnight; G3 - Colgate Plax Alcohol Free; and G4 - Colgate Plax Whitening). The initial hardness and roughness readings (T1) were measured and then the specimens were stored in 2 mL of mouthwash for 12 h (T2) and 24 h (T3). The data were analyzed with repeat-measures two-way ANOVA and Tukey's test (α = 5%). Regardless of the type of solution and time of exposure, there was no statistical difference for roughness between the resins (p = 0.44). G4 and G8 presented higher roughness means than G1, G3, G5 and G7, after 12 and 24 hours of immersion. For Knoop microhardness analysis, there was a significant reduction for all groups after 12 hours and 24 hours. We conclude that the mouthwashes containing hydrogen peroxide and/or alcohol decrease the microhardness of the resins tested; however, the mouthwash containing hydrogen peroxide had a higher deleterious effect on roughness.

Descriptors: Composite Resins; Mouthwashes; Hardness; Surface Properties.

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Introduction

Resin composites are made up of a polymeric matrix, filler particles, and silane-coupling agent that links the matrix to fillers.[1,2] As a polymer-based material, the composites may undergo degradation inside the oral environment, resulting in alterations of the mechanical properties.[3,4]

The degradation is a complex mechanism dependent on the polymeric matrix, filler particles, and other processes, such as water uptake inside the matrix,[5,6] thermal and mechanical cycling, and crack propagation and attenuation.[7,8] In the clinical situation, composite degradation cannot be assigned to a single factor or chemical substance; rather, it is the result of complex reactions among different factors.[9] Water is directly related to the composite organic matrix deterioration. The absorption of this liquid results in a widespread process within the composite resin ma-

trix that causes its degradation and results in lower physical and mechanical properties,[10,11] above all related to resin hardness and roughness.[12]

Mouthwashes are widely used to prevent and control caries and periodontal diseases, and are frequently used, even without professional prescription. The formulation of these mouthwashes consists of water, antimicrobial agents, salts, and, in some cases, alcohol,[13] and the different concentrations of these substances can affect the pH of mouthwashes. However, the effects of such components on the composite resins polymeric matrix are widely discussed.[14-16]

In addition to conventional products containing alcohol, mouthwashes containing hydrogen peroxide have been marketed. However, in this case, besides hydrogen peroxide at low concentration, these mouthwashes contain alcohol in their composition. It is known that acid solutions may cause changes in the organic composition of resin composites.[17] It is speculated that the high oxidative power of bleaching agents, in contact with organic molecules, could change the polymeric bonds and make the composite more susceptible to degradation.[18] Furthermore, changes throughout the inorganic phase may decrease the material's physical properties, such as microhardness and roughness.[17,18]

Previous studies[19-23] indicated that the literature is still controversial about the influence of mouthwashes on the mechanical and physical properties of composites, even in terms of their hardness and roughness. Thus, the aim of this *in vitro* study was to analyze the effects of mouthwashes with different compositions, after two immersion times, on the surface roughness and hardness of composites with different compositions of the organic matrix. The investigated null hypotheses were: (1) the composition of mouthwashes tested does not interfere with Knoop microhardness and surface roughness of resin composites; (2) the time of immersion in mouthwashes does not interfere with Knoop microhardness and surface roughness of resin composites tested; (3) the resin composites tested present no roughness and hardness differences.

Materials and Methods

Two resin composites were selected: 4 Seasons (A3 - Ivoclar Vivadent, Schaan, Liechtenstein) and Esthet X (A3 - Dentsply, Milford, DE, USA). The composition of the resin composites is described in Table 1. Three mouthwashes were chosen: Plax Overnight®, Plax Alcohol free®, Plax Whitening® (Colgate-Palmolive Ltda, São Bernardo do Campo, São Paulo, Brazil) and distilled water was used as control (Table 2), resulting in 8 groups (n = 10) (Table 3). To measure the pH, 20 ml of each substance was added to a beaker, and the pH was obtained with a glass pH electrode 1.5 cm in diameter (PROCYON model AS 720 (Procyon Instrum. Científica Ltda, São Paulo, SP, Brazil) and each value is described in Table 2.

Cylindrical specimens were prepared in teflon ring molds (6.0 mm ∅ and 2 mm height). A polyester strip was placed on a glass slab (Dentsply, Petrópolis, Rio de Janeiro, Brazil) and teflon matrix. After filling the mold to excess, the material surface was covered with another polyester strip and a glass slide, and compressed with a device (500 g) for 20 s to accommode the resin better and remove the excess material. All the resin composite specimens were light-activated with a quartz-tungsten-halogen unit Luting XL3000 (3M do Brasil, Sumaré, SP, Brazil) with 400 mW/cm² for 40 seconds, and stored in distilled water for 24 h at 37 °C. After this period, all specimens were finished with silicon carbide papers (Arotec, Cotia, SP, Brazil - 1200 grit) under constant water cooling.

Initially, the first reading (T1) of surface roughness was made with a profilometer roughness tester (Mitutoyo, Surftest 211; São Paulo, SP, Brazil) in

Table 1 - Composite resin, composition and batches.

Resin	Batch	Composition
Esthet X	0708000242	UDMA, Bis-GMA, Bis-EMA, TEGDMA 60 vol% of fluor-aluminum boron barium silicate glass with particles sized 0.6 - 0.8 μm and silica nanoparticles (0.04 nm)
4 Seasons	K27335	Bis-GMA, TEGDMA, UDMA 76 wt% of barium glass filler, trifluor terbium, Ba-Al fluor silicate glass and dispersed silica with filler particles sized 0.04 - 3.0 μm, and filler average size of 0.6 μm

Table 2 - Mouthwashes, pH, compositions and batches.

Solution	Batch	pH	Composition
Colgate Plax Overnight	BR121A	6.04	Water, glycerin, alcohol (8%), propylene glycol, sorbitol, PEG-40 hydrogenated castor oil, aroma, sodium benzoate, cetylpiridinium chloride, sodium fluoride, sodium saccharin, CI 42090.
Colgate Plax Alcohol free	BR122A	4.96	Water, glycerin, propylene glycol, sorbitol, PEG-40 hydrogenated castor oil, aroma, phosphoric acid, sodium benzoate, cetylpiridinium chloride, sodium fluoride, sodium saccharin, CI 42090
Colgate Plax Whitening	BR122A	3.74	Water, sorbitol, ethylic alcohol (8%), hydrogen peroxide (1.5%), polaxamere 338, polissorbate 20, methyl salicilate, menthol, sodium saccharine, CI 42090

three equidistant marks, and the surface hardness reading was made with a microdurometer (HMV, Shimadzu, Tokyo, Japan). Five consecutive and equidistant readings were obtained (50 μm) per specimen to evaluate Knoop hardness (KHN), using a 50 g load, with a dwell time of 15 s.

Each experimental group prepared was stored in 2 mL of the respective mouthwashes for 12 h, which was reported to be equivalent to 1 year of daily mouthwash use, 2 min per day[15]. The samples in the mouthwashes were kept at 37°C throughout the study and were shaken on an orbital rotational table MA 140 CFT (Marconi Equipamentos, Piracicaba, SP, Brazil) every 3 h, to provide homogeneity. After this period, the specimens were washed with abundant water and submitted to new roughness and hardness readings (T2). They were then re-immersed in solutions for a 12-hour period, totaling 24 hours of immersion. The specimens were then rinsed with abundant water and submitted to new roughness and hardness readings (T3) under the same experimental conditions. The control groups were tested in the same way as the experimental groups, after immersion in distilled water.

The obtained results for microhardness and roughness were tabulated, and the homogeneity was verified by Kolmogorov-Smirnov and Shapiro-Wilk tests. After observation of these parameters, a two-way Analysis of Variance with repeated-measures was performed. When the statistical significance was verified, the Tukey test was applied in order to compare results (α = 5%). The statistical analysis was carried out with SAS 9.1 software (SAS Institute, Cary, NC, USA).

Table 3 - Group distribution, according to the composite resin and solution tested.

4 Seasons		Esthet X	
G1	Distilled water	G5	Distilled water
G2	Plax Overnight®	G6	Plax Overnight®
G3	Plax Alcohol free®	G7	Plax Alcohol free®
G4	Plax Whitening®	G8	Plax Whitening®

Results

Knoop Microhardness

The analysis of variance showed the interaction between the variables "composite resins", "immersion times" and "solutions" ($p = 0.017$). Means and standard deviations as well as results of Tukey test are presented in Table 4. There was a significant microhardness reduction for all groups after 12 hours (except for G5) and 24 hours. T3 differed from T2 for groups G2, G4, G6 and G8. G6 presented a higher hardness only for G2, in times T2 and T3, and G8 in time T3.

Surface roughness

The two-way Analysis of Variance ANOVA showed the interaction between the variables "immersion times" and "solutions" ($p < 0.001$). There were no statistical differences between resins, regardless the type of solution and time ($p = 0.44$). Table 5 presents means and standard deviation values for the factors type of mouthwash and time, and the results of Tukey's test. G4/G8 presented higher roughness means with statistical differences for G1, G3, G5 and G7, after 12 and 24 hours of immersion, and for G2 and G6 after 24 hours. G3 and G7

Table 4 - Means Hardness (standard deviation) according of the type of resin, mouthwash and immersion time (KNH).

Composite	Group	Time		
		T1	T2	T3
4 Seasons	G1	55.27 (2.4) Aa	52.27 (1.5) Ba	51.89 (1.5) Ba
	G2	53.19 (2.2) Aa	40.88 (1.8) Bc*	32.97 (1.5) Cc*
	G3	55.00 (2.0) Aa	43.33 (2.5) Bb	42.46 (2.0) Bb
	G4	55.30 (2.4) Aa	38.76 (2.0) Bd	31.88 (1.9) Cc*
Esthet X	G5	54.91 (2.6) Aa	52.65 (2.0) Aba	50.49 (2.5) Ba
	G6	54.52 (2.8) Aa	45.65 (2.3) Bb*	35.14 (1.2) Cc*
	G7	55.16 (2.3) Aa	44.96 (3.3) Bb	42.66 (2.8) Bb
	G8	54.69 (2.8) Aa	38.37 (1.9) Bc	35.73 (2.0) Cc*

Means followed by different letters (capital letters in the horizontal and lower case letters in the vertical) differ between them in the Tukey's test ($p < 0.05$). * Significant difference between the two tested resins.

statistically differed from G1 and G5 after 24 hours. As far as groups G2, G3, G4, G6, G7 and G8 are concerned, there were differences between immersion times in that T3 differed from T1. T3 differed from T2 only for G2, G4, G6 and G8.

Discussion

According to the results of this study, the first null hypothesis that the different mouthwashes do not interfere with the Knoop hardness and surface roughness of composites was rejected. Furthermore, the roughness values increased according to the immersion time. Unlike the roughness results, the microhardness values decreased with immersion in the mouthwashes. The second null hypothesis of the present study was therefore rejected.

The chemical composition of resin composites may interfere in the susceptibility to softening and degradation.[24,25] The resin 4 Seasons presented more alteration in hardness after immersion in mouthwashes tested, compared to Esthet-X. The first resin contains Bis-GMA and UDMA in its composition, and it is known that these monomers are more susceptible to softening after exposure to chemical agents.[19] However, the composite Esthet-X contains Bis-EMA, and reduced amount of TEGDMA, and these characteristics promote better resistance of the composite resin to the action of chemical substance.[26]

The third null hypothesis that the roughness and hardness of the resins tested would be similar was partially accepted, since the resins present different

Table 5 - Roughness means (standard deviation) according to immersion time in different mouthwash solutions (Ra).

Groups	Time		
	T1	T2	T3
G1/G5	0.29(0.03) Aa	0.31(0.02) Ac	0.31(0.03) Ad
G2/G6	0.31(0.04) Ca	0.34(0.02) Bab	0.37(0.04) Ab
G3/G7	0.30(0.03) Ba	0.32(0.02) Abc	0.33(0.04) Ac
G4/G8	0.31(0.04) Ca	0.37(0.05) Ba	0.41(0.02) Aa

Means followed by different letters (capital letters in the horizontal and lower case letters in the vertical) differ between them in the Tukey's test ($p < 0.05$).

microhardness but similar roughness. The presence of Bis-EMA incorporated in the organic matrix of Esthet X and distribution, type and size of filler particles[27,28] probably resulted in higher hardness values compared to the composite 4 Seasons. For roughness, no differences were observed between the resins, which suggest that the increased roughness is directly related to the composition, pH and immersion time in solution.[11]

Furthermore, the pH of the tested solutions provides another possible preponderant factor for the composite matrix degradation. Analyzing the composition of mouthwashes in Table 2, we observe that Plax Alcohol Free contains phosphoric acid and Plax Whitening contains hydrogen peroxide. The measurement of pH of these mouthwashes was 4.96 and 3.74, respectively. Compared to distilled water (pH = 5.5) the higher acidity may have altered the polymeric matrixes of the resin composite by catalysis of ester groups from dimethacrylate monomers

present in their compositions (Bis-GMA, Bis-EMA, UDMA or TEGDMA). The hydrolysis of these ester groups may have formed alcohol and carboxylic acid molecules, which accelerate the degradation of the resin composites, due to the decrease of pH inside the resin matrix.[25]

Another study[29] showed that the low pH of solutions may induce phenomena of sorption and hygroscopic expansion, due to the production of methacrylic acid, the result of the degradation process of the enzymatic hydrolysis.

Using the solubility parameters of polymers in alcohol solvents, the higher softening of resin composites occurred with 75% ethanol, when compared to those of 100%, 50%, 25%, or 0% ethanol. However, the effect of the chemical agent on the hardness of the composite resin is material-dependent.[23] Another study has also reported that beverages containing 9% or more of ethanol might lead to softening of the restorative material matrix, interfering in the polymer-filler particle interface, increasing the wear.[30] However, considering that the specimens were immersed in solutions with up to 8% alcohol concentration, the solubility of the material resulted in detachment of filler particles[25] and probably caused degradation of the material surface, resulting in a decrease of hardness and an increase of roughness.

Clinically, the mouthwashes' effects on resin composites may be different according to some factors, such as acquired biofilm, food habits, beverages, and oral care products, which cannot be reproduced *in vitro*. Those factors, acting together or in isolation, may interfere with the physical and mechanical properties of the materials, influencing the durability of the restorative treatment.

Conclusions

In conclusion, the results of this study showed that those mouthwashes containing alcohol or hydrogen peroxide present a higher potential to change the superficial roughness and hardness of the tested composites. The length of immersion time affected the Knoop microhardness and surface roughness of the composites tested, above all among mouthwashes containing alcohol or hydrogen peroxide, and alcohol-free mouthwashes affected the hardness and roughness of composites more than distilled water. Composite resins presented differences only in hardness properties after immersion in mouthwashes containing alcohol or hydrogen peroxide.

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