Effects of 6 Months of Aging in Water on Hardness and Surface Roughness of Two Microhybrid Dental Composites

Rafael Ratto de Moraes, DDS,[1] José Laurindo Machado Marimon,[2] Luis Felipe Jochims Schneider, DDS, MS,[1] Mário Alexandre Coelho Sinhoreti, DDS, MS, PhD,[3] Lourenço Correr-Sobrinho, DDS, MS, PhD,[3] & Márcia Bueno, DDS, MS, PhD[4]

[1] Graduate Student, Department of Restorative Dentistry, Dental Materials Area, Piracicaba School of Dentistry, State University of Campinas
[2] Undergraduate Student, Department of Restorative Dentistry, School of Dentistry, Federal University of Pelotas
[3] Professor, Department of Restorative Dentistry, Dental Materials Area, Piracicaba School of Dentistry, State University of Campinas
[4] Professor, Department of Restorative Dentistry, School of Dentistry, Federal University of Pelotas

Keywords
Aging; dental composites; hardness; surface roughness.

Correspondence
Prof. Dr. Márcia Bueno, Department of Restorative Dentistry, School of Dentistry, Federal University of Pelotas, 457 Gonçalves Chaves St., Centro, 96015-560 Pelotas, RS, Brazil. E-mail: mbuenop@terra.com.br

Accepted January 22, 2007.

doi: 10.1111/j.1532-849X.2007.00295.x

Abstract

Purpose: This study assessed the effect of 6 months of aging in water on surface roughness and surface/subsurface hardness of two microhybrid resin composites.
Materials and Methods: Filtek Z250 and Charisma were tested. Cylindrical specimens were obtained and stored in distilled water for 24 hours or 6 months, at 37°C. For Knoop hardness evaluation, the specimens were transversely wet-flattened, and indentations were made on surface and subsurface layers. Data were submitted to three-way ANOVA and Tukey's test ($\alpha \leq 0.05$). Surface roughness baseline measurements were made at 24 hours and repeated after 6 months of storage. Data were submitted to repeated measures ANOVA and Tukey's test ($\alpha \leq 0.05$).
Results: Surface hardness (KHN, kg/mm^2) means (± standard deviation) ranged from 55 ± 1 to 49 ± 4 for Z250 and from 50 ± 2 to 41 ± 3 for Charisma, at 24 hours and 6 months, respectively. Subsurface means ranged from 58 ± 2 to 61 ± 3 for Z250 and from 50 ± 1 to 54 ± 2 for Charisma, at 24 hours and 6 months. For both composites, the aged specimens presented significantly softer surfaces ($p < 0.01$). For the subsurface hardness, alteration after storage was detected only for Charisma, which presented a significant rise in hardness ($p < 0.01$). Z250 presented significantly harder surface and subsurface layers in comparison with Charisma. Surface roughness (Ra, μm) means ranged from 0.07 ± 0.00 to 0.07 ± 0.01 for Z250 and from 0.06 ± 0.01 to 0.07 ± 0.01 for Charisma, at 24 hours and 6 months, respectively. For both composites, no significant roughness alteration was detected during the study ($p = 0.386$).
Conclusions: The 6-month period of storage in water presented a significant softening effect on the surfaces of the composites, although no significant deleterious alteration was detected for the subsurface hardness. In addition, the storage period had no significant effect on the surface roughness of the materials.

Resin-based materials are widely used in dentistry because of their good esthetic appearance, ease of handling, and ability to establish a bond to hard dental tissues. To achieve successful clinical performance, these materials are required to have long-term durability, which is strongly influenced not only by the intrinsic characteristics of the materials, but also by the environment to which they are exposed.[1-3] The oral cavity is a thermal cycled, warm, and moist environment, and it has been shown that water has the ability to degrade composites by hydrolyzing inorganic filler particles,[4-6] weakening polymer matrixes,[4,7] and debonding filler-matrix interfaces.[6,8] These processes may, in the short or long term, present a deleterious effect on the polymeric network, modifying its structure physically and chemically.[9,10]

Physical characteristics are of critical importance when deciding on suitable materials,[11-13] because they strongly influence the clinical durability of restorations. One of the most important properties is the material hardness, which correlates well to compressive strength, abrasion resistance, and degree of conversion.[14] Low hardness values are usually linked to poor wear resistance[15] and susceptibility to scratching,[16] which can compromise fatigue strength and lead to restoration failures. Furthermore, resin surface degradation and inorganic filler leaching may cause microscopic changes that could alter material smoothness over the course of time, and hence interfere with both esthetics and health. Rougher surfaces are a predisposing factor for bacteria adhesion, plaque maturation, periodontal disease, and extrinsic staining.[17]

Table 1 Materials used

Resin composite	Lot code	Composition*
Z250	14081	BisGMA, UDMA, BisEMA, TEGDMA, zirconia, silica (0.01–3.5 μm, 60 vol%)
Charisma	010047	BisGMA, TEGDMA, AlF, Ba and SiO_2 glass particles (0.02–2 μm, 64 vol%)

*Personal communication.

Because literature regarding the effect of aging on composites presents controversial findings, further assessment is warranted. Lloyd[18] observed no significant changes in fracture toughness of composites after extended storage. Conversely, Ferracane et al[7] described reduction of up to 30% in surface hardness and in fracture toughness of composites aged in water, which is in line with other investigations.[19,20] Furthermore, little is known about the influence of aging on the surface smoothness of resin-based restoratives. Munack et al[20] reported that polyacid-modified composites displayed low surface roughness values, varying between 0.03 and 0.08 μm, throughout a 12-month storage period, even though a decrease in surface hardness of up to 32% was detected. Thus, the aim of this study was to evaluate the effect of a 6-month aging period in water on surface roughness and surface/subsurface hardness of two microhybrid resin composites.

Materials and methods

Two commercial microhybrid resin composites, shade A2, were evaluated: Charisma (Heraeus Kulzer, Hanau, Germany) and Filtek Z250 (3M ESPE, St. Paul, MN). Material composition is presented in Table 1. These composites were selected because they present similar filler load but different organic matrix components. For each material, 31 specimens were obtained. The resin composites were placed in a cylindrical-shaped stainless steel mold (10 mm inner diameter × 3-mm thick) in three increments, each one light-activated for 40 seconds (XL 3000, 3M ESPE; 500mW/cm^2). A transparent polyester strip and a glass slide were placed against the bottom and top layers, and hand pressure was applied prior to light-activation. The strips were then removed and the specimens immediately stored in light-proof containers at 37°C, for 24 hours. Thereafter, polishing was performed with medium, fine, and superfine aluminum oxide discs (Sof-Lex system, 3M ESPE), followed by a 30-second air/water spray washing.

Sixteen specimens per composite were randomly assigned to the hardness evaluation. Specimens were stored in distilled water at 37°C (pH = 5.8) for 24 hours or 6 months. During the storage period, the water was changed every month. After each period, the specimens were embedded in epoxy resin and transversely wet-flattened by means of 400-, 600-, and 1200-grit silicon carbide papers, to expose both surface and subsurface layers. A Knoop diamond on a microhardness tester (HMV-2, Shimadzu, Tokyo, Japan) was used, and a 50-g load was applied through the indenter for a dwell time of 15 seconds. For each sample, five indentations were made on the irradiated surface and another five indentations were made at 1-mm deep, with a constant 1.5-mm distance between each indentation. The Knoop hardness number (KHN, kg/mm^2) for both surface and subsurface layers of each specimen was recorded as the average of the five readings. Data were submitted to three-way ANOVA, with a split-plot design for comparisons within the same specimen (surface vs. subsurface), followed by Tukey's test ($\alpha \leq 0.05$).

The 15 remaining specimens were assigned to the surface roughness evaluation. Readings were performed using a previously calibrated surface profilometer (Surfcorder SE1200, Kosaka Lab., Tokyo, Japan), equipped with a diamond stylus (0.5-μm tip radius) and accurate to 0.01 μm. Baseline measurements were made at 24 hours, and repeated after 6 months. The storage protocol followed was the same as the one conducted for the hardness assessment. The specimens were rotated through the profilometer clockwise at random angles. Five traverses of the stylus were made across the diameter for each sample. The mean roughness parameter (Ra, μm) for each specimen was recorded as the average of the five readings. Data were submitted to repeated measures ANOVA and Tukey's test ($\alpha \leq 0.05$).

Results

Table 2 displays the results for the hardness assessment. After the 6-month storage period, both composites presented significantly softer surfaces in comparison with the 24 hour samples ($p < 0.01$). On the other hand, for the subsurface hardness, no significant alteration was detected when comparing Z250 24-hour to aged specimen; Charisma presented a significantly harder subsurface layer after the storage period ($p < 0.01$). Furthermore, with the exception of 24-hour Charisma, irrespective of the composite tested or the evaluation period, hardness at the subsurface was found to be significantly higher than surface hardness ($p < 0.01$). In addition, Z250 presented significantly harder surface and subsurface layers compared to Charisma ($p < 0.01$). Table 3 shows the results for the surface roughness evaluation. Both composites presented similar results. No significant alteration between before and after the immersion period was detected ($p = 0.386$).

Table 2 Means ± standard deviation for hardness (KHN, kg/mm^2)

Resin composite	Surface		Subsurface	
	24 hours	6 months	24 hours	6 months
Z250	55 ± 1 B,a	49 ± 4 C,a	58 ± 2 A,a	61 ± 3 A,a
Charisma	50 ± 2 B,b	41 ± 3 C,b	50 ± 1 B,b	54 ± 2 A,b

Means followed by distinct capital letters in the same line, and small letters in the same column are significantly different ($p < 0.01$).

Table 3 Means ± standard deviation for surface roughness (Ra, μm)

Resin composite	24 hours	6 months
Z250	0.07 ± 0.00	0.07 ± 0.01
Charisma	0.06 ± 0.01	0.07 ± 0.01

No significant differences were detected throughout the study (p = 0.386).

Discussion

The present results reveal that both composites presented significant surface softening after the 6-month storage period, corroborating previous investigations.[7,19,20] This can be explained by water serving as a plasticizing molecule within the composite matrix.[7] It is well-recognized that the water uptake process is the main factor responsible for the appearance and propagation of interfacial debonding, matrix cracking, superficial flaws, and filler particle dislodgment in the course of time.[5-7] Indeed, this reduction does not rely solely on physical or chemical polymer matrix degradation, as the literature also presents evidence of filler and filler/matrix interface dissolution.[5,6] The whole hydrolytic degradation mechanism is a diffusion rate-dependent process, influenced by polymer type, filler load and type, and surface treatment of the particles.[8] When composites are immersed in water, the resin matrix swells, reducing the frictional forces between polymer chains.[7] Furthermore, tensile stresses are generated at the resin-filler interfaces, straining the bonds in the inorganic component and increasing the frictional forces between filler and resin matrix, facilitating pull-out of fillers.[5] On the other hand, hardness at the subsurface did not decrease with aging; however, when assessing the subsurface layer, aged Charisma specimens were shown to be significantly harder in comparison with 24-hour specimens. A rise in hardness as a function of aging is probably explained by increased monomer conversion and/or additional post-curing cross-linking reactions in the resin phase in the course of time.

Although both materials presented significant surface softening as a function of storage, aged Z250 specimens presented a decrease in hardness of around 10%, while Charisma specimens showed a reduction of around 18%. Although it is uncertain whether these magnitudes predict different clinical performances, an explanation for this difference depends on the organic component of each material (Table 1). Finer and Santerre[10] observed that the urethane coupling of the BisGMA molecule enhances the stability of the composite, and Braden and Davy[9] verified that BisGMA-based resins undergo greater water sorption compared with urethane-based ones. Furthermore, Watts et al[14] showed that a urethane-modified BisGMA composite exhibited greater physical stability in water and lower water uptake. In addition, Charisma presents higher amounts of TEGDMA, and the literature also reports that increasing the TEGDMA content in resin matrix systems leads to an increase in water uptake, as this monomer presents higher hydrophilicity when compared with BisGMA and UDMA.[8]

The resin top layer, low-polymerized due to oxygen inhibition, is a much weaker phase than the bulk of the cured material, and its presence would probably yield lower hardness values. Therefore, in the present study all sample surfaces were polished prior to storage. Nonetheless, hardness at the subsurface was significantly higher than hardness at the top layer for both composites, either before or after the storage period, which is in agreement with Nomoto et al.[12] Indeed, Reinhardt[13] reported corresponding findings for conversion of double bonds, even when the specimens were prepared in an argon atmosphere. The author explains this phenomenon by the fact that, in the bulk of the material, a free radical is surrounded in three dimensions by possible reaction partners, while a radical located at the interface can find possible partners to react only on one side of a hypothetical sphere centered on the free radical. An additional explanation is that, during photoactivation procedures, the temperature rise in the deeper layers of the composite is greater than at the surface, due to reduced heat conduction,[11] and it has been demonstrated that even small increases in temperature may give rise to significant increases in hardness.[14]

Although the composites tested here do not present significant differences as regards the inorganic filler load, Z250 samples were shown to be significantly harder in comparison with Charisma specimens, regardless of the layer examined or the evaluation period ($p < 0.01$). Differences in the organic matrix component provide a possible explanation for this finding; Kawai et al[16] and Söderholm et al[21] described increased wear resistance for urethane-based resins in comparison with BisGMA-based ones. Moreover, Yamaga et al[22] observed that the content of functional urethane monomer is directly related to hardness and fracture toughness parameters. Furthermore, the two composites present differences with regard to filler morphology; irregular-shaped particles are present in Charisma, whereas Z250 presents predominantly round fillers.[23] Indeed, Kim et al[24] reported that the composites with round particles showed improved hardness and flexural strength properties compared with those containing irregular-shaped particles. These results are probably related to the fact that the spherical shape improves particle packing and generally enhances the fracture strength of the composite, as mechanical stresses tend to concentrate on irregularities of the filler/matrix interface, such as filler angles and protuberances.[23] In addition, Z250 presents larger filler particles than Charisma, which could also be related to the present results.

The hardness results indicate that the storage period presented a significant detrimental effect on the surfaces of the composites. As a probable consequence, the inorganic particles are no longer provided with a stable structure, which could predispose to filler dislodgment and elution. Therefore, one could expect that the decreased surface hardness should be accompanied by increased surface roughness. Indeed, water sorption reduces the hoop stresses around fillers, which facilitates the plucking-out of particles. Nonetheless, although filler leaching probably occurred during the storage period, both composites showed no significant alteration in surface roughness between the periods before and after the immersion ($p = 0.386$). Corroborating this finding, Munack et al[20] reported that, despite the decreased surface hardness observed, the surface roughness of polyacid-modified composites did not change during a 12-month storage period.

In the present study, the aging process was carried out by soaking the specimens in distilled water, at 37°C, for a period of

6 months, and previous studies have used similar experimental designs;[7,19] however, the artificial saliva storage medium could be considered a more clinically relevant environment. Nonetheless, Turssi et al,[1] when evaluating the influence of storage media upon the micromorphology of resin-based materials, described similar results for distilled water and artificial saliva, and Yap et al[3] reported equivalent degradation for composites after exposure to either water or artificial saliva. Furthermore, during the course of the experiment, the water was changed monthly, and an enhanced degradation could be expected if the storage medium had been more frequently renewed.

With regard to future research, assessment of the components desorbed into water during storage and chemical analyses to show the presence of water on the surfaces would allow a further evaluation of the hydrolytic process of dental composites. In addition, measurement of specimen weight changes during the test, as well as dehydration of the specimens at the end of the experiment, to observe if they return to the original values, could indicate whether the present results are related to a water-only effect or a combined effect of organic matrix components loss over time as well.

In summary, the current study raises a question about the harmful influence of water on the surface hardness of dental composites. Nonetheless, it is unknown whether these changes could take place to the same extent in the mouth, and whether these alterations indicate a poor clinical performance for any composite. However, in the oral environment, parameters such as pH changes, salivary enzymes, and ionic composition of food, beverages, or saliva may operate either alone or in combination with other factors, such as sliding, abrasion, or fatigue, to interfere with the hydrolytic process.[2] Therefore, the long-term clinical and in vitro performance of dental composites needs further evaluation.

Conclusions

The 6-month period of storage in water presented a significant softening effect on the surface of the composites ($p < 0.01$), whereas no significant deleterious alteration was detected for hardness at the subsurface layer. On the other hand, the storage period had no significant effect on the surface roughness of the materials ($p = 0.386$).

Acknowledgment

This study was partially supported by Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS), Brazil, Grant 03/51069.4.

References

1. Turssi CP, Hara AT, Serra MC, et al: Effect of storage media upon the surface micromorphology of resin-based restorative materials. J Oral Rehabil 2002;29:864-871
2. Wu W, McKinney JE: Influence of chemicals on wear of dental composites. J Dent Res 1982;61:1180-1183
3. Yap AU, Tan SH, Wee SS, et al: Chemical degradation of composite restoratives. J Oral Rehabil 2001;28:1015-1021
4. Calais JG, Soderholm KJ: Influence of filler type and water exposure on flexural strength of experimental composite resins. J Dent Res 1988;67:836-840
5. Soderholm KJ: Degradation of glass filler in experimental composites. J Dent Res 1981;60:1867-1875
6. Soderholm KJ, Zigan M, Ragan M, et al: Hydrolytic degradation of dental composites. J Dent Res 1984;63:1248-1254
7. Ferracane JL, Berge HX, Condon JR: In vitro aging of dental composites in water—effect of degree of conversion, filler volume, and filler/matrix coupling. J Biomed Mater Res 1998;42:465-472
8. Ferracane JL: Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater 2006;22:211-222
9. Braden M, Davy KW: Water absorption characteristics of some unfilled resins. Biomaterials 1986;7:474-475
10. Finer Y, Santerre JP: The influence of resin chemistry on a dental composite's biodegradation. J Biomed Mater Res A 2004;69:233-246
11. Asmussen E, Peutzfeldt A: Influence of specimen diameter on the relationship between subsurface depth and hardness of a light-cured resin composite. Eur J Oral Sci 2003;111: 543-546
12. Nomoto R, Uchida K, Hirasawa T: Effect of light intensity on polymerization of light-cured composite resins. Dent Mater J 1994;13:198-205
13. Reinhardt KJ: Unconverted double bonds and interface phenomena in composite materials. Dtsch Zahnarztl Z 1991;46:204-208
14. Watts DC, McNaughton V, Grant AA: The development of surface hardness in visible light-cured posterior composites. J Dent 1986;14:169-174
15. Say EC, Civelek A, Nobecourt A, et al: Wear and microhardness of different resin composite materials. Oper Dent 2003;28:628-634
16. Kawai K, Iwami Y, Ebisu S: Effect of resin monomer composition on toothbrush wear resistance. J Oral Rehabil 1998;25:264-268
17. Bollen CM, Lambrechts P, Quirynen M: Comparison of surface roughness of oral hard materials to the threshold surface roughness for bacterial plaque retention: a review of the literature. Dent Mater 1997;13:258-269
18. Lloyd CH: The fracture toughness of dental composites. III. The effect of environment upon the stress intensification factor (KIC) after extended storage. J Oral Rehabil 1984;11:393-398
19. Martos J, Osinaga PW, Oliveira E, et al: Hydrolytic degradation of composite resins: effects on the microhardness. Mater Res 2003;6:599-604
20. Munack J, Haubert H, Dogan S, et al: Effects of various storage media on surface hardness and structure of four polyacid-modified composite resins ("compomers"). Clin Oral Investig 2001;5:254-259
21. Soderholm KJ, Lambrechts P, Sarrett D, et al: Clinical wear performance of eight experimental dental composites over three years determined by two measuring methods. Eur J Oral Sci 2001;109:273-281
22. Yamaga T, Sato Y, Akagawa Y, et al: Hardness and fracture toughness of four commercial visible light-cured composite resin veneering materials. J Oral Rehabil 1995;22:857-863
23. Sabbagh J, Ryelandt L, Bacherius L, et al: Characterization of the inorganic fraction of resin composites. J Oral Rehabil 2004;31:1090-1101
24. Kim KH, Ong JL, Okuno O: The effect of filler loading and morphology on the mechanical properties of contemporary composites. J Prosthet Dent 2002;87:642-649