

Hydrolytic stability of dental composites: one-year aging effect on surface roughness and surface/subsurface hardness

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Abstract: The effect of one-year aging on roughness and hardness of microhybrid composites was investigated. Z250 (3M ESPE) and Charisma (Heraeus Kulzer) were tested. Specimens were stored in distilled water at 37 °C for 24 hours, 6 months or 1 year. Knoop hardness indentations were performed on surface and subsurface (1 mm deep). Data were submitted to three-way ANOVA and Tukey's test ($p \leq 0.05$). Surface roughness (R_a , μm) was measured at 24 hours, 6 months and 1 year. Data were submitted to Repeated Measures ANOVA and Tukey's test ($p \leq 0.05$). Surface hardness ranged from 55.0 to 48.6 and 44.0 for Z250, and from 49.8 to 40.7 and 39.5 for Charisma, at 24 hours, 6 months and 1 year, respectively. Subsurface hardness ranged from 57.8 to 60.9 and 54.2 for Z250, and from 50.4 to 54.3 and 50.7 for Charisma, at 24 hours, 6 months and 1 year. After 6 months, both composites presented softer surfaces ($p < 0.01$). When comparing 6-month and 1-year, only Z250 showed a decrease in hardness ($p < 0.05$). For the subsurface, a decrease in hardness after 1 year was observed ($p < 0.05$). Generally, hardness at the subsurface was higher than surface hardness ($p < 0.01$), and Z250 was harder than Charisma ($p < 0.01$). Roughness ranged from 0.53 to 0.52 and 0.52 for Z250, and from 0.52 to 0.56 and 0.56 for Charisma, at 24 hours, 6 months and 1 year, with no significant differences among the materials ($p = 0.231$).

Keywords: Aging; composite resins; hardness; inorganic particles; surface properties.

Resumo: O efeito do envelhecimento por um ano na rugosidade e dureza de compósitos micro-híbridos foi investigado. Z250 (3M ESPE) e Charisma (Heraeus Kulzer) foram testados. Espécimes foram armazenados em água destilada a 37 °C por 24 horas, 6 meses ou 1 ano. Endentações de dureza Knoop foram feitas na superfície e subsuperfície (1 mm). Os dados foram submetidos à ANOVA e teste de Tukey ($p \leq 0,05$). A rugosidade da superfície (R_a , μm) foi mensurada em 24 horas, 6 meses e 1 ano. Os dados foram submetidos à ANOVA de Medidas Repetidas e teste de Tukey ($p \leq 0,05$). A dureza superficial variou de 55,0 para 48,6 e 44,0 para Z250, e de 49,8 para 40,7 e 39,5 para Charisma, em 24 horas, 6 meses e 1 ano, respectivamente. A dureza da subsuperfície variou de 57,8 para 60,9 e de 54,2 para Z250, e de 50,4 para 54,3 e 50,7 para Charisma. Depois de 6 meses, os compósitos apresentaram menor dureza superficial ($p < 0,01$). Comparando 6 meses e 1 ano, apenas Z250 mostrou menor dureza ($p < 0,05$). Para a subsuperfície, foi observada diminuição na dureza após 1 ano ($p < 0,05$). Em geral, a dureza na subsuperfície foi maior que na superfície ($p < 0,01$), e Z250 foi mais dura que Charisma ($p < 0,01$). A rugosidade variou de 0,53 para 0,52 e 0,52 para Z250, e de 0,52 para 0,56 e 0,56 para Charisma, em 24 horas, 6 meses e 1 ano, sem diferenças significativas entre os materiais ($p = 0,231$).

Palavras-chave: Envelhecimento; resinas compostas; dureza; partículas inorgânicas; propriedades de superfície.

Introduction

Resin-based materials are increasingly being used in dentistry. For a successful, long-lasting clinical performance, long-term durability is required. The durability depends upon not only the characteristics of the materials^{1,2}, but also on the environment to which they are exposed^{1,3-5}. The oral cavity is a thermal cycled, moist environment, and water has shown the ability to degrade composites by hydrolyzing inorganic particles⁶, weakening polymer matrixes³ and debonding filler-matrix interfaces⁷. These processes may, in the short or long term, present a deleterious effect in the polymeric network, modifying its structure chemically and physically¹.

Amongst the properties interfering with the clinical durability of composite fillings, the hardness, which correlates well to compressive strength and conversion degree, has critical importance. Low hardness values are usually linked to poor wear resistance⁸ and susceptibility to scratching⁹, and can compromise fatigue strength and lead to restoration failures. Furthermore, resin surface degradation and inorganic filler leaching may cause microscopic changes that could alter the material smoothness over the course of time, and hence interfere with both aesthetics and health¹⁰.

Because literature presents controversial findings with regard to the effect of aging on composites, further assessment is warranted. For instance, Lloyd¹¹ observed no significant changes in fracture toughness of composites after extended storage, while Ferracane et al.³ described reduction of up to 30% in fracture toughness after water aging. Furthermore, little is known about the influence of aging on the surface smoothness of resin-based restoratives. Thus, the aim of this study was to evaluate the effect of a one-year aging period on surface roughness and surface/subsurface hardness of resin composites. The hypotheses tested were that (1) the immersion period would present a significant softening effect on the composites, and that (2) an increase in surface roughness of the materials would be observed after storage.

Material and method

Two commercial microhybrid resin composites, shade A2, were evaluated: Charisma (Heraeus Kulzer, Hanau, Germany) and Filtek Z250 (3M ESPE, St. Paul, MN, USA). Materials composition is presented in Table 1. These composites were selected because they present similar filler load but different organic matrix components. For each material, 39 specimens were obtained. The composites were placed into a cylindrical-shaped stainless steel mold (10 mm inner diameter x 3 mm thick) in three increments, and each increment was light-activated for 40 seconds (XL3000; 3M ESPE, 500 mW.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-curing. The strips

Table 1. Materials used in the study

Resin Composite	Lot Code	Composition
Filtek Z250	14081	Bis-EMA, UDMA, Bis-GMA, TEGDMA, silica/zirconia (0.01-3.5 µm, 60 vol%)
Charisma	010047	Bis-GMA, TEGMA, Al-F-Ba-Si glass particles (0.02-2 µm, 64 vol%)

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 seconds air/water spray washing.

Twenty-four samples per composite were randomly assigned to the hardness evaluation. Specimens were stored in distilled water (pH = 5.8) at 37 °C for 24 hours, 6 months or 1 year. During the storage period, the water medium was changed every month. After each period, the specimens were embedded in cold-cure epoxy resin and transversally wet-flattened with 400, 600 and 1200grit SiC papers, in order 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 performed on the irradiated surface and another five indentations at 1 mm deep, with a constant 1.5 mm distance between each indentation. The Knoop hardness number (KHN) for the surface and subsurface layers of each specimen was recorded as the average of the five readings. Data were submitted to Three-Way ANOVA (material vs. storage time vs. layer), with a split-plot design for comparisons within the same specimen (surface vs. subsurface), followed by Tukey's test ($p \leq 0.05$).

The fifteen remaining specimens were assigned to the surface roughness evaluation. Readings were performed using a previously calibrated surface profilometer (Surf-corder 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 and 1 year. 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 ($p \leq 0.05$).

Additionally, a washing technique was performed in order to remove the resin matrix and examine the morphology and size of the inorganic fillers. A sample of 250 mg of each material was dissolved in 4 mL of absolute acetone and centrifuged for 5 minutes at 1000 rpm (Excelsa Baby I 206; Fanem, São Paulo, SP, Brazil). The process was carried out three times using acetone and three other times using chloroform. The remaining filler particles were placed in 2 mL of absolute ethanol, smeared on a metal stub and dried at 37 °C during 4 hours. Thereafter, the filler bearing stubs were coated with gold and SEM examination was performed (JSM 5600LV; Jeol Inc., Peabody, MA, USA).

Result

Table 2 shows the results for the hardness assessment. The statistical analysis showed that the factors 'material' ($p < 0.001$), 'storage time' ($p < 0.001$) and 'layer' ($p = 0.009$) were all significant, but no significant interactions among them were detected ($p \geq 0.156$). After the 6-month storage period, both composites presented significantly softer surfaces in comparison to 24 hours ($p < 0.01$). When comparing 6-month and 1-year aged groups, no significant differences were detected for Charisma, whereas a significant decrease in KHN was observed for Z250 ($p < 0.05$).

On the other hand, for the subsurface layer, no significant alteration was detected when comparing 24 hours and 6-month aged specimens, except for Charisma, which presented significantly harder after aging ($p < 0.01$). However, after 1 year, a decrease in subsurface KHN in comparison to 6 months was detected for both composites ($p < 0.05$). Moreover, irrespective of the composite tested or the evaluation period, KHN at the subsurface was found to be significantly higher than in the surface ($p < 0.01$), except for Charisma at 24 hours. Furthermore, Z250 presented significantly harder than Charisma ($p < 0.01$), except for the subsurface layer after 1 year.

Table 3 shows the results for the surface roughness evaluation. No significant alterations were detected throughout the study ($p = 0.231$), irrespective of the resin composite or the immersion period. Moreover, the SEM analysis revealed noticeable differences between the composites with regard to the inorganic fillers' morphology: irregular-shaped particles

were observed for Charisma, whereas Z250 presented predominantly round filler particles, as shown in Figure 1.

Discussion

The first hypothesis tested might be accepted, as both composites presented significant surface softening after the 6-month storage period, corroborating previous

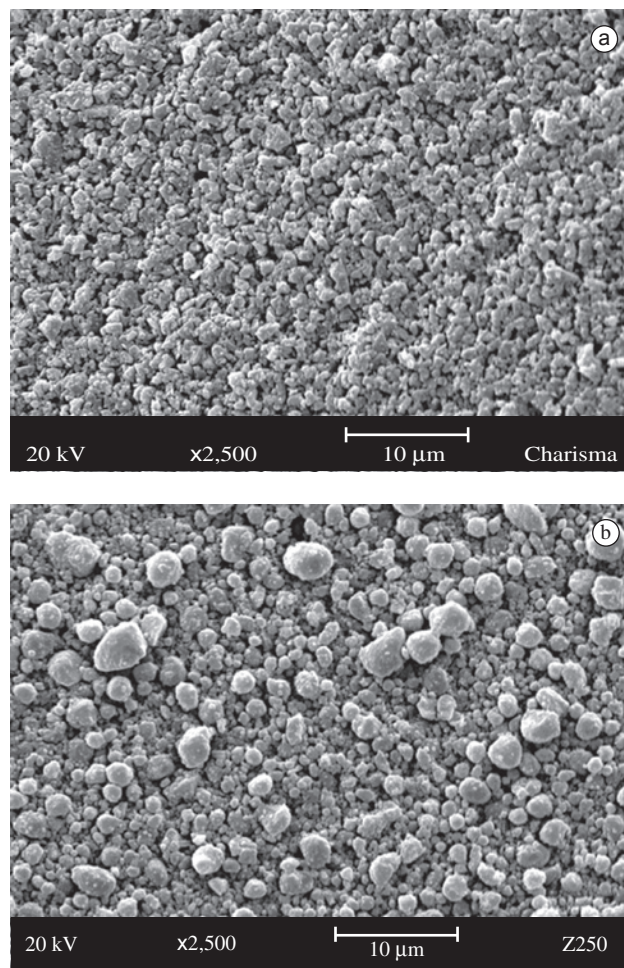


Figure 1. SEM pictures of inorganic fillers' morphology. a) Charisma: irregular-shaped particles can be noted; b) Z250: Round particles are predominantly present.

Table 2. Means (standard deviation) for Knoop hardness (KHN)

Material	Surface			Subsurface		
	24 hours	6 months	1 year	24 hours	6 months	1 year
Z250	55.0(1.4) ^{B,a}	48.6(3.7) ^{C,a}	44.0(2.5) ^{D,a}	57.8(2.4) ^{A,a}	60.9(3.4) ^{A,a}	54.2(2.3) ^{B,a}
Charisma	49.8(2.0) ^{B,b}	40.7(2.7) ^{C,b}	39.5(3.3) ^{C,b}	50.4(1.1) ^{B,b}	54.3(2.3) ^{A,b}	50.7(3.9) ^{B,a}

Means followed by the different capital letters in the same line, and small letters in the same column, are significantly different at $p \leq 0.05$

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

Material	24 hours	6 months	1 year
Z250	0.53(0.08)	0.52(0.08)	0.52(0.09)
Charisma	0.52(0.08)	0.56(0.12)	0.56(0.08)

No significant differences were detected throughout the study ($p = 0.231$)

investigations^{3,12}. This can be explained by water serving as a plasticizing molecule within the material^{1,3}. The water uptake process is the main responsible for the appearance and propagation of matrix cracking, superficial flaws, interfacial debonding and filler particle dislodgment over the course of time^{1,3,7}. These alterations do not rely solely on physical or chemical polymer degradation, but also on filler and filler/matrix interface dissolution⁷. The whole hydrolytic mechanism is diffusion rate dependent, influenced by polymer type, filler load and type, and surface treatment of the particles⁷. When composites are immersed in water, the organic matrix swells, reducing the frictional forces between polymer chains³. Also, tensile stresses are generated at the resin-filler interface, straining the bonds in the inorganic component and altering the frictional forces between filler and resin matrix, facilitating pull-out of fillers¹.

Although both materials presented surface softening after 6 months, Z250 presented a decrease in hardness of around 10%, while Charisma showed a reduction of around 18%. This might be related to the chemistry of the resin components. Previous studies show that the urethane coupling of Bis-GMA enhances the stability of the composite, and that Bis-GMA-based resins show higher water sorption than urethane-based materials^{2,13}. In addition, Charisma has higher amounts of TEGDMA, increasing the water sorption because of the higher hydrophilicity of this monomer¹. However, after 1 year, no significant decrease in hardness was detected for Charisma, whereas Z250 showed its lowest hardness values throughout the study. This outcome suggests that, probably due to the lower water affinity of Z250, the 6-month aging period was insufficient to completely decrease the hardness values. In fact, the access of water in a polymeric network is dependent upon the diffusion coefficient of water, which is dictated by the formulation of the material. Likewise, for both composites, hardness at the subsurface significantly decreased only after 1 year.

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. In corroboration, Reinhardt¹⁴ 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 three-dimensionally surrounded 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 photo-activation procedures, the temperature rise in the deeper layers of the composite is greater than at the surface, due to reduced heat conduction¹⁵, and it has been demonstrated that even small increases in temperature may give rise to significant increases in hardness¹³.

Although the composites tested here do not present significant differences as regards the inorganic filler load, Z250 samples were generally harder than Charisma specimens. This could be related to differences in the organic component. Soderholm et al.¹⁶ described increased wear resistance for urethane-based composites compared with Bis-GMA-based materials, and Yamaga et al.¹⁷ showed that the content of functional urethane monomer is directly related to the hardness parameter of the corresponding polymer. Furthermore, the two composites present differences with regard to fillers' morphology: irregular-shaped particles were observed for Charisma, whereas Z250 showed predominantly round fillers. Kim et al.¹⁸ reported that composites with round particles might show improved hardness compared with those containing irregular-shaped fillers. This is probably related to the fact that the spherical shape improves particle packing and generally enhances the mechanical strength of the composite, as stresses tend to concentrate on irregularities of the filler/matrix interface, such as filler angles and protuberances.

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. Nonetheless, although filler leaching has probably occurred during the storage period, both materials showed no significant alteration in surface roughness over the course of time. Therefore, the second hypothesis tested might be rejected. In corroboration, Munack et al.¹² 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, and other studies have conducted similar experimental design^{3-5,19}. However, the artificial saliva storage medium could be considered a more clinically relevant environment. Nonetheless, Turssi et al.⁴, when evaluating the influence of storage media upon the morphology of resin-based materials, described

similar results for distilled water and artificial saliva, and Yap et al.⁵ reported equivalent degradation for composites after exposure to either water or artificial saliva. In addition, for future researches, assessment on the components desorbed into water during storage, and chemical analyses to show the presence of water on the surfaces, would allow a further evaluation on the hydrolytic process of dental composites, as could indicate whether the present outcomes are related to a water-only effect or a combined effect of organic matrix components loss over time as well.

In conclusion, the current study shows a material and time-dependent harmful influence of water on hardness of dental composites. Nonetheless, it is unknown whether these changes could take place to the same extent in the mouth, or 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. Therefore, the long-term clinical and in vitro performance of dental composites needs further evaluation.

Conclusion

The 6-month aging period presented a significant softening effect on the surface of both composites, whereas only the 1-year period influenced the subsurface hardness. The 1-year storage period had no significant effect on the surface roughness of the materials.

Acknowledgments

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