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Physicomechanical properties of different nanohybrid composites after aging: color stability, flexural strength, and microhardness

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Aim: To evaluate the physicomechanical properties of different hybrid composites (Charisma Diamond - CD, Aura - AU, NT Premium - NT, Opallis - OP, Filtek Z250 – Z250) after 6 months of aging in distilled water. **Methods:** Discs were fabricated and color measurements were performed after 24 hours and at 7, 30, and 180 days. Flexural strength was determined using the three-point bending test. For the microhardness test, the specimens were flattened to obtain polished and flat surfaces and indentations. The results for ΔE and microhardness were analyzed by two-way repeated-measures ANOVA and Tukey's HSD test. The flexural strength results were analyzed by two-way ANOVA and Tukey's test (α=0.05). **Results:** The ΔE values for composite resins varied in the following order: CD (3.54)a < Z250 (4.70)ab < AU (4.95)ab < OP (5.20)ab < NT (6.23)b. ΔE values were lower for 24 h (3.84)a < 7 days (4.43)ab < 30 days (4.93)b. The highest values were observed after 180 days (ΔE = 6.54)c. The flexural strength of composite resins varied in the following order: CD (89.17 MPa)a < Z250 (73.06 MPa)b < OP (60.30 MPa) c < NT (51.28 MPa)c < AU (23.77 MPa)d. Flexural strength values were significantly higher for 24 h (68.62 MPa)a < 180 days (51.40 MPa)b. The microhardness of composite resins varied in the following order: Z250 (112.05)a < CD (102.15)ab < OP (92.04) bc < NT (87.77)d < AU (87.68)d. Microhardness was significantly higher for 180 days (113.44)a < 24 h (78.21)b. **Conclusion:** The microhybrid (Z250) and one of the nanohybrid composites (CD) performed better. The color stability and flexural strength of all tested composites decreased with storage time.

Keywords: Mechanical phenomena. Hardness. Flexural strength. Color.

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Introduction

Nanotechnology is a reality in restorative dentistry and has been available in dental composite resins with nanoscale particles (1-100 nm size range). In the last decade, formulations of microhybrid universal composites (with filler size averaging 0.4 to 1.0 μm) have been modified to include nanoparticles and possibly pre-polymerized resin fillers (nanofiller clusters). This group of dental composite resins is identified as nanohybrids[1]. It is known that the mechanical and optical properties of composite resins are highly dependent on the type, volume percentage, and particle size of inorganic fillers[1,2].

For esthetic rehabilitations, the color stability of composite resins is crucial. Discoloration of these materials has been attributed to factors such as oxidation in the tertiary amine or oxidation of unreacted pendant methacrylate groups[3,4]. Color stability can also depend on the different fillers used in these materials[3,5].

Additionally, direct composite restorations need to be functional immediately and for longer periods of time. When placed in the oral environment, composite resins are constantly in contact with humidity. The interaction with saliva can impair flexural strength[6] and lead to fractures, resulting in functional and esthetic problems.

The hardness of composite resins, defined as resistance against permanent indentation or penetration on the surface of the restoration, is another significant property associated with composite materials. The composition of each material can result in low- or high-hardness composites[7] and, consequently, lead to restoration fracture and eventual failure.

Thus, the aim of this study was to evaluate the physicomechanical properties (color stability, flexural strength, and microhardness) of different hybrid composites after 6 months of aging in distilled water. The tested hypotheses were that: i) there would be differences between the hybrid composites regarding the three physicomechanical properties; and ii) storage time would influence the physicomechanical properties of the evaluated composites.

Material and Methods

Five hybrid composite resins were used in the present study. The composition of each composite resin is described in Table 1.

All specimens were prepared under controlled humidity (55 ± 5%), temperature (23 ± 1 ºC), and illumination conditions. Ten disc specimens (5 mm in diameter and 1 mm in thickness) were prepared for each material. Each specimen was obtained by inserting the composite resin in a Teflon mold, keeping it pressed between two 1-mm thick glass slides, separated by Mylar strips, under finger pressure. The specimens were photoactivated with a LED-curing unit (Radii-cal, SDI, Victoria, Australia) at an irradiance of 1,200 mW/cm^2. The irradiance of the light source had been previously measured by a radiometer (LED Demetron, Kerr, Middleton, WI, USA). After removal from the mold, the irradiated surface of the specimens was subjected to polishing procedures with a one-step polishing system (EasyShine, Kulzer, Hanau, Germany).

Table 1. Compositions of materials used in this study

Group	Material	Composition
AU	Aura (SDI, Bayswater, Australia) – shade E2	Matrix: UDMA, Bis-GMA, Bis-EMA, TEGDMA Filler: 20 nm silica and 400 nm silanated barium glass; 81% wt (65% vol%)
CD	Charisma Diamond (Kulzer, Hanau, Germany – shade A2)	Matrix: TCD-DI-HEA, Bis-GMA, TEGDMA Filler: Ba, Al, F glass (0.02–2.0 μm) and colloidal silica (0.02–0.07 μm); 81% wt (64% vol%)
NT	NT Premium (Coltene/Whaladent, Altstätten, Switzerland) – shade A2E	Matrix: Bis-GMA, Bis-EMA, TEGDMA Filler: silica nanoparticles (10 - 40 nm, 10.2 wt%) and aluminasilicate glass (71.3 wt%); total 81.5 wt% (61 vol%)
OP	Opallis (FGM, Joinville, Brazil) – shade EA2	Matrix: Bis-GMA, Bis-EMA, TEGDMA, UDMA Filler: silanized barium-aluminum silicate glass and silica (40 nm - 2.0 μm), with a mean size of 0.5 μm; 78.5% wt% (58.0 vol%)
Z250	Filtek Z250 (3M ESPE, St. Paul, USA) – shade A2	Matrix: Bis-GMA, Bis-EMA, UDMA, TEGDMA Filler: zirconia, silica (0.01 - 3.5 μm), 78 wt%, 60 vol%

Bis-GMA: bisphenol-A glycol dimethacrylate; Bis-EMA: ethoxylated bisphenol-A dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; UDMA: urethane dimethacrylate

The color measurements were performed with a spectrophotometer (EasyShade Advance, Vita Zahnfabrik, Bad Sackingen, Germany) according to the CIELab coordinates under a standardized white background. Initial measurement was performed 1 hour after polymerization (baseline). The specimens were immersed in distilled water at 37 °C in dark canisters. The color parameters were measured again after 24 hours and at 7, 30, and 180 days. The CIELab coordinates were used to calculate the color difference (ΔE) between the "before" (baseline) and "after" periods. The ΔE for each experimental time was calculated using the equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

where ΔL, Δa, and Δb are the differences in the respective values before and after aging.

Twenty specimens were made for each composite resin for the evaluation of flexural strength. A split stainless steel mold was used to obtain specimens with 10 x 2 x 1 mm. The composite resins were inserted into the mold and excess material was removed. Half of the specimens were polished and then stored in distilled water at 37 °C for 24 hours. The other half was stored for 180 days in distilled water at 37 °C, in dark canisters. Flexural strength was determined using the three-point bending test on a universal testing machine (EMIC DL 2000, São José dos Pinhais, PR, Brazil) at a crosshead speed of 0.5 mm/min. Flexural strength (S), in MPa, was calculated by the following formula:

$$S = 3Fl/2bh^2$$

where F is the fracture load (N), l is the span length (6 mm), and b and h are, respectively, the width and height of the specimen (mm).

The same 10 specimens used for color stability evaluation were tested for microhardness using a Vickers hardness tester (D-89610; Bareiss Prüfgerätebau GmbH, Oberdischingen, Germany). Three indentations were made in each sample by applying a 50 g load with a dwell time of 10 s. A distance of at least 1 mm was allowed between indentations.

The results for ΔE and microhardness were analyzed by two-way repeated-measures ANOVA and Tukey's HSD test. The results of flexural strength were analyzed by two-way ANOVA and Tukey's HSD test. Correlation between flexural strength and Vickers microhardness was determined by Pearson's coefficient (R). The level of significance was set at 0.05 for all analyses.

Results

Means and standard deviations for ΔE values are presented in Table 2. There were significant differences in color stability for composite resins ($p = 0.0027$), time ($p < 0.0001$), and two-way interaction ($p < 0.0001$). The ΔE values for composite resins varied in the following order: CD $(3.54)^{a}$ < Z250 $(4.70)^{ab}$ < AU $(4.95)^{ab}$ < OP $(5.20)^{ab}$ < NT $(6.23)^{b}$. When the storage times were considered, ΔE values were lower for 24 h $(3.84)^{a}$ < 7 days $(4.43)^{ab}$ < 30 days $(4.93)^{b}$. The highest values were observed after 180 days (ΔE = $6.54)^{c}$.

Means and standard deviations for flexural strength are presented in Table 3. Significant differences were observed for composite resins ($p < 0.0001$), time ($p < 0.0093$) and two-way interaction ($p < 0.0001$). The flexural strength for composite resins varied in the following order: CD (89.17 MPa)^{a} < Z250 (73.06 MPa)^{b} < OP (60.30 MPa)^{c} < NT (51.28 MPa)^{c} < AU (23.77 MPa)^{d}. As for time, flexural strength was significantly higher for 24 h (68.62 MPa)^{a} < 180 days (51.40 MPa)^{b}.

Table 3 also shows the Vickers microhardness values for composite resins tested after storage for 24 h and 180 days. Significant differences were observed for composite resins, time, and two-way interaction ($p < 0.0001$). The microhardness for composite resins varied in the following order: Z250 $(112.05)^{a}$ < CD $(102.15)^{ab}$ < OP $(92.04)^{bc}$ < NT $(87.77)^{d}$ < AU $(87.68)^{d}$. In terms of time, microhardness was significantly higher at 180 days $(113.44)^{a}$ < 24h $(78.21)^{b}$.

Table 2. Means and standard deviations for the DE values.

Composite resin	DE 24h	DE 7 days	DE 30 days	DE 180 days
AU	2.24 ± 1.15^{aA}	6.48 ± 1.84^{bB}	5.71 ± 1.88^{aB}	5.38 ± 3.14^{abB}
CD	2.90 ± 1.99^{abA}	2.16 ± 1.33^{aA}	4.45 ± 2.27^{aA}	4.66 ± 2.80^{aA}
NT	5.05 ± 1.85^{abA}	5.60 ± 2.32^{aA}	6.24 ± 2.25^{aA}	8.02 ± 2.25^{abA}
OP	2.95 ± 1.88^{abA}	4.47 ± 1.84^{abA}	4.78 ± 2.43^{aA}	8.61 ± 4.14^{bB}
Z250	6.26 ± 2.25^{bA}	3.31 ± 1.64^{abA}	3.30 ± 1.06^{aA}	5.94 ± 1.61^{abA}

*Values followed by the same lower case letters (in columns) and capital letters (in lines) are statistically similar ($p > 0.05$).

Table 2A. Means and standard deviations for the DE values.

Composite resin	DE
AU	4.95^{AB}
CD	3.54^{A}
NT	6.23^{B}
OP	5.20^{AB}
Z250	4.70^{AB}

*Values followed by the same letters are statistically similar ($p > 0.05$).

A moderate positive correlation was observed for Vickers microhardness and flexural strength at both 24 hours and 180 days (Pearson's correlation coefficient of 0.623 and 0.618, respectively) (Figure 1)

Table 3. Means and standard deviations for flexural strength and Vickers microhardness after storage of 24h and 180 days.

Composite resin	Flexural strength (MPa)		Vickers microhardness (kgf/mm²)	
	24h	180 days	24h	180 days
AU	29.65 ± 2.74^{dA}	15.69 ± 4.67^{cA}	71.83 ± 5.38^{abA}	95.61 ± 4.27^{bA}
CD	107.19 ± 9.02^{aA}	69.36 ± 21.27^{aB}	93.71 ± 29.35^{aA}	111.53 ± 14.45^{abA}
NT	54.66 ± 7.22^{cA}	48.49 ± 14.60^{bA}	62.49 ± 10.78^{bB}	102.94 ± 14.47^{bA}
OP	71.26 ± 16.15^{bcA}	44.32 ± 16.97^{bB}	60.14 ± 3.64^{bB}	127.49 ± 13.97^{aA}
Z250	78.85 ± 23.85^{bA}	67.27 ± 67.54^{abB}	93.38 ± 6.51^{aB}	132.80 ± 14.60^{aA}

*For each property, values followed by the same lower case letters (in columns) and capital letters (in lines) are statistically similar ($p > 0.05$).

Table 3A. Means and standard deviations for flexural strength and Vickers microhardness.

Composite resin	Flexural strength (MPa)	Vickers microhardness (kgf/mm²)
AU	23.77^{D}	87.68d
CD	89.17^{A}	102.15^{ab}
NT	51.28^{C}	87.77^{d}
OP	60.30^{C}	92.04^{bc}
Z250	73.06^{B}	112.05^{a}

*For each property, values followed by the same letters are statistically similar ($p > 0.05$).

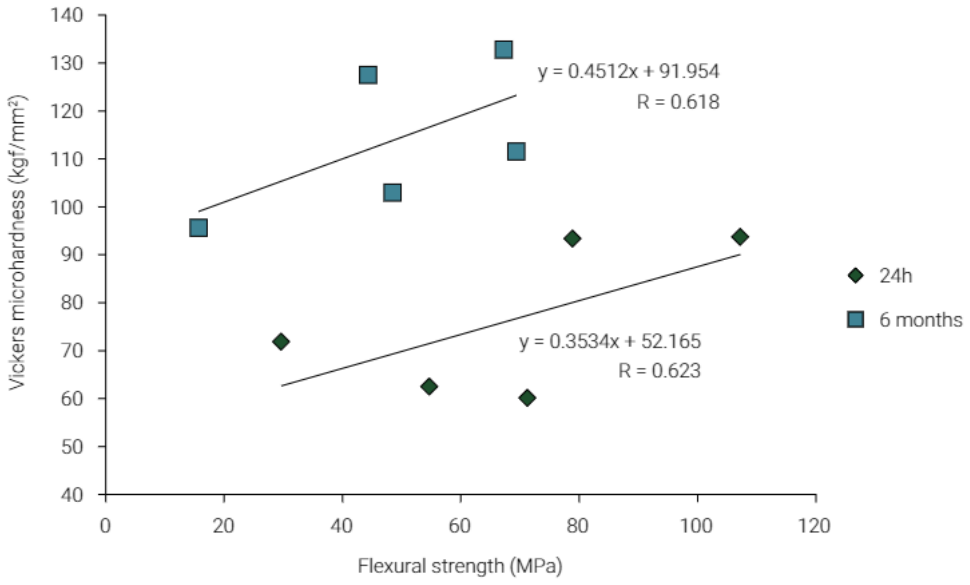

Figure 1. Correlation plot between Vickers microhardness and flexural strength for 24h and 180 days of water storage.

Discussion

Long-term performance of dental composites is determined by their physicomechanical properties. The first tested hypothesis – that there would be differences between the evaluated nanohybrid composites regarding the three physicomechanical properties – was accepted. In the present study, the microhybrid composite resin (Z250) and one of the nanohybrid composite resins (CD) presented better results (higher color stability, flexural strength, and Vickers microhardness). However, nanohybrid composite resins AU and NT presented the lowest values for flexural strength and microhardness.

These differences in their physicomechanical properties can be attributed to differences in composition, as the materials vary in resin matrix and filler type/loading/particle size. However, the proportions of the components in each material are exclusive, and the differences among composite resins from different manufacturers are not specified when commercial brands are compared. As can be seen in Table 1, the monomers are similar for all tested materials, but their proportions might vary.

Other studies have also shown that microhybrid Filtek Z250 resin has higher mechanical properties, surface hardness, and highest degree of conversion, but lower surface roughness than other composite resins[8]. The flexural strength of a restorative material is considered essential for preventing repair or failure processes. Charisma Diamond presents a different resin matrix, which might explain the better results obtained in the present study when compared with the other materials.

Filler particle-related features, such as the concentration and size of the filler reinforcement and resin formulation, determine the surface hardness of the composite[9,10]. Thus, the materials with better filler loading can achieve higher wear resistance[9,10]. Also, zirconia and silica fillers in Filtek Z250 have greater hardness and less solubility when compared with fillers in NT Premium and Aura[8,10]. Finally, higher microhardness is observed in composites with uniform distribution of filler content when compared to composites with a mixture of irregular and rounded filler particles[8,11].

The second tested hypothesis – that the storage time would influence the physicomechanical properties of the evaluated composites – was accepted. For flexural strength, all values decreased after 180 days of storage. The greatest difference in flexural strength was seen in AU (-47.08%), followed by OP (-37.80%) and CD (-35.29%). For Z250 and NT, flexural strength after storage decreased 14.68% and 11.29%, respectively. After 6 months in water, the microhybrid composite resin (Z250) and one of the nanohybrid composite resins (CD) presented higher flexural strength when compared with the other materials tested in the same period.

It is widely known that composite materials degrade as a result of water storage[12,13] and that their mechanical properties can be reduced because of plasticization and degradation of the matrix/filler interfaces owing to water sorption and flow of long-chain polymers[14].

The incorporation of TEGDMA into the resin matrix might increase water uptake because of the hydrophilic properties of this monomer when compared to Bis-GMA and UDMA[15,16]. Given the increased flexibility of TEGDMA, cross-linking density is also

decreased. Therefore, leaching of the unreacted TEGDMA monomer could be related to lower mechanical properties[17].

Unlike flexural strength, which was significantly affected by the aging procedure, hardness, in the present study, increased after 6 months of water storage. The literature is not consistent regarding the influence of aging on hardness. There are studies reporting that hardness might increase[18] or decrease[19,20] after aging, or even that aging by water storage or thermocycling does not significantly affect hardness[21].

As seen in the results of the present study, a positive correlation between flexural strength and hardness was found (moderate positive Pearson's correlation coefficient ranging from 0.618 to 0.623). According to the literature, this correlation was expected because both properties are associated with the complex stresses developed within the material. Hardness measurements are related to compressive or shear stresses, and flexural strength is commonly associated with maximum tensile stress[21]. In the present study, a moderate positive correlation was observed for Vickers microhardness and flexural strength at both 24 hours and 180 days (Pearson's correlation coefficient of 0.623 and 0.618, respectively).

Immersion in water caused changes in the color of all tested materials. The water absorbed by the resin matrix can cause filler matrix debonding and hydrolytic degradation of the material[4,22,23]. Also, ΔE values showed a predisposition to go up as the immersion period increased, suggesting that the color of the material would tend to change over long-term clinical use[3,4,24-27].

Therefore, based on the results of the present study, it can be concluded that the evaluated physicomechanical properties were material-dependent. The microhybrid (Z250) and one of the nanohybrid composites (CD) performed better. The color stability and flexural strength of all tested composites decreased with storage time. A moderate positive correlation was observed for Vickers microhardness and flexural strength at both 24 hours and 180 days.

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