

Correlation between water uptake and biaxial flexural strength in restorative composites

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ABSTRACT | Though aging of resin composites has been the subject of several investigations, the correlation between strength and water uptake has not been established. Therefore, the purpose of the present study was to determine whether a statistically significant correlation exists between biaxial flexural strength and weight gain due to water uptake for two commercial restorative composites, one methacrylate-based and one silorane-based. Discs (15 mm in diameter by 1 mm thick) were made with either Filtek Z250 or Filtek Silorane (both from 3M ESPE) and dry-stored for 30 days. Then, they were weighed in an analytical balance and immersed in distilled water at 37°C for 1, 2, 5, 7, 30 or 60 days (n = 10). After the immersion period, the discs were re-weighed and immediately fractured on a “piston-on-three-ball” device. Mass gain (in percentage) and biaxial flexural strength data were subjected to two-way ANOVA / Tukey test and Pearson’s correlation analysis ($\alpha = 5\%$). Mass gain was similar for both composites in a given storage period, and did not vary significantly between one and seven days. For Filtek Z250, biaxial strength decreased gradually with prolonged immersion, while, for Filtek Silorane, it decreased abruptly between 30 and 60 days. Statistically significant correlations were found between strength and mass gain for both composites. However, a stronger correlation was found for Filtek Z250 ($r = -0.706$, $p < 0.001$) compared to Filtek Silorane ($r = -0.361$, $p < 0.01$). Therefore, it was possible to conclude that strength is linearly related to water uptake and this correlation is material-dependent.

DESCRIPTORS | Composite Resins; Silorane Resins; Water; Dental Materials / analysis.

RESUMO | **Correlação entre sorção de água e resistência à flexão biaxial em compósitos restauradores** • Embora o envelhecimento de compósitos resinosos tenha sido o objeto de investigação de diversos estudos, a correlação entre resistência e sorção de água não foi estabelecida. Portanto, o objetivo do presente estudo foi verificar se existe uma correlação estatisticamente significativa entre a resistência à flexão biaxial e o ganho de peso devido a sorção de água para dois compósitos comerciais, um à base de metacrilatos e outro à base de silorano. Discos (15 mm de diâmetro por 1 mm de espessura) foram confeccionados com Filtek Z250 ou Filtek Silorane (ambos da 3M ESPE) e armazenados a seco por 30 dias. Em seguida, eles foram pesados em uma balança analítica e imersos em água destilada a 37°C por 1, 2, 5, 7, 30 ou 60 dias (n = 10). Após o período de imersão, os discos foram novamente pesados e imediatamente fraturados em um dispositivo do tipo “pistão sobre três esferas”. Os dados de ganho de massa (em porcentagem) e resistência à flexão biaxial foram submetidos a ANOVA de dois fatores / teste de Tukey e teste de correlação de Pearson ($\alpha = 0,05$). O ganho de massa foi semelhante para os dois compósitos para um dado período de armazenamento e não variou significativamente entre um e sete dias. Para o Filtek Z250, a resistência diminuiu gradualmente com a imersão prolongada, ao passo que, para o Filtek Silorane, ela diminuiu abruptamente entre 30 e 60 dias. Correlações estatisticamente significativas foram encontradas entre resistência e ganho de massa para ambos os compósitos. Entretanto, uma correlação mais forte foi encontrada para o Filtek Z250 ($r = -0,706$, $p < 0,001$) comparado com o Filtek Silorane ($r = -0,361$, $p < 0,01$). Portanto, foi possível concluir que a resistência é linearmente dependente do ganho de água e que essa correlação é material-dependente.

DESCRITORES | Resinas Compostas; Resinas de Silorano; Água; Materiais Dentários / análise.

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INTRODUCTION

The effect of solvent immersion on the mechanical properties and unreacted monomer elution of resin composites has been extensively studied since their early days.^{1,2} The reason for such concern is self-evident, as the consequences of these occurrences are numerous, ranging from esthetical issues (discoloration and change in surface texture) up to, most importantly, severe reductions in mechanical properties and potential biocompatibility issues.³ In spite of the constant improvements in composite formulation over the last decades that resulted in improved clinical performance, composite longevity in humid environments remains a critical issue,⁴ as clinical studies report bulk failure as one of the main causes of failure in composite restorations.⁵

Composite degradation in the oral environment is the result of water molecules penetrating the polymer chains, releasing residual monomers and weakening the secondary bonds, as well as the degradation of the filler-matrix interface.^{6,7} Water sorption initiates as soon as the composite comes into contact with oral fluids and, according to *in vitro* studies, a significant change in mass is detected between three to five days of immersion.^{3,6} The amount of absorbed water depends on the composite organic and inorganic composition, as well as its degree of conversion. For example, the more densely reticulated and more heterogeneous is the polymer structure, the higher is the sorption.⁸ In unfilled monomer blends, the reduction in tensile strength observed during a 12-month immersion period was directly related to resin hydrophilicity.⁹ The type and size of filler was also demonstrated to influence the amount of water absorbed by a composite. Experimental composites containing barium glass absorb more water than those containing quartz; in addition, only the barium glass particle size was inversely related to the amount of water absorbed.¹⁰

The effect of prolonged water immersion on the mechanical properties of resin composites has been extensively studied. Flexural strength of dimethacrylate-based composites determined by three-point bending showed reductions between 16% and 24% after 30 days in water.^{11,12} After 90 days, dimethacrylate-based composites presented reductions between 25% and 65%, while a silorane-based composite showed a 15% decrease in strength.¹³ In general, flexural strength, elastic modulus and fracture toughness tend to stabilize after six months of immersion.⁶

The vast majority of aging studies involving resin composites focuses on the reduction in properties as a function of storage periods, and do not try to correlate the actual water uptake with the reduction in mechanical properties. Notwithstanding, the relationship between water uptake overtime and the change in mechanical properties of restorative polymeric materials was investigated in a few studies. In one of these studies, commercial adhesive systems containing hydrophilic monomers showed almost linear correlations between water uptake and elastic modulus in discs with 6 mm in diameter and 0,5 mm thickness, where after three days of immersion a mass gain between 6% and 21% corresponded to a decrease in elastic modulus between 21% and 42%.¹⁴ Another study followed the change in mass and flexural properties of a commercial composite during nine months of immersion in artificial saliva, not finding significant variations in any of the variables.¹⁵

Specimens with dimensions similar to those adopted for the water sorption/solubility test by ISO 4049 (15 mm diameter, 1 mm thickness)¹⁶ can be used to determine the biaxial flexural strength of composites. In this case, the surface exposed to the immersion media is approximately three times larger compared to the bar-shaped specimens used in three-point bending tests. Moreover, the specimen in the biaxial strength test is less susceptible

to processing flaws, such as edge defects that act as stress raisers. As a consequence, data scattering is decreased and specimen failure stress is a closer estimate of the actual tensile stresses.¹⁷

Therefore, the purpose of this study was to determine whether a correlation exists between biaxial flexural strength and water sorption in two commercial resin composites, one dimethacrylate-based and one silorane-based, measured in the same specimen. The null hypothesis was that there is no statistically significant correlation between weight gain and the reduction in mechanical strength for the tested materials.

MATERIALS AND METHODS

Table 1 shows the materials tested in this study and the respective formulations. Both composites are made by the same manufacturer (3M ESPE, St. Paul, MN, USA); the A2 shade was chosen for testing.

Disc-shaped specimens 15 mm in diameter by 1 mm thickness were made using a split stainless steel mold filled in a single increment. After insertion, the composite was covered by a piece of mylar strip and a microscopy glass slide, and light-cured using a LED unit (Flash Light, Discus Dental, Culver City, CA, USA) with nominal irradiance of 1,200 mW/cm² for 30 seconds. The tip of the light guide was kept at a 5 mm distance from the composite surface in order to allow for an irradiated area equivalent to the diameter of the specimen. After the first 30-second exposure,

the specimen was removed from the mold and the opposite surface was irradiated for another 30 seconds.

Excess composite was removed with 220 grit sandpaper. Then, the specimen was weighed in an analytical balance, with resolution of 0.1 mg (Mettler Toledo, model XS105, Greifensee, Switzerland) and transferred to a desiccator at 37°C under vacuum until reaching a constant mass (m_1), which took approximately 30 days. The dimensions of the disc were measured with a digital caliper (Digimatic Caliper CD-6"OS, Mitutoyo, Japan) and then the specimen was immersed in 20 mL of distilled water at 37°C for one of the following intervals (n = 10): 1, 2, 5, 7, 30 or 60 days. Its mass after immersion (m_2) was used to calculate the percent mass gain using the following formula:

$$\text{mass gain} = 100 \times (m_2 - m_1) / m_1$$

After determining the mass of the specimen following immersion, the disc was immediately fractured under flexural loading in a "piston-on-three-balls" device positioned in a universal testing machine (model 5565, Instron Corp., Canton, MA, USA). The biaxial flexural test followed the ISO 6872 standard.¹⁸ The testing device has three steel spheres with 2.5 mm in diameter placed 120° distant from each other on a 10 mm diameter circumference. The specimen was positioned concentrically with this circumference and the load was applied by a flat piston with 1.2 mm diameter, at a

Table 1 | Materials tested in the study (information provided by the manufacturer).

Material	Matrix composition	% filler (by volume)	Batch
Filtek Z250	Bis-GMA (2,2-bis[4-(2-hydroxy-3-methylacryloxypropoxy)-phenyl]propane), TEGDMA, Bis-EMA6 (bisphenol A hexaethoxylated dimethacrylate) and UDMA (urethane dimethacrylate)	60	N377933BR
Filtek Silorane	3,4-epoxycyclohexylethycyclo polymethylsiloxane	55	N383595

crosshead speed of 0.5 mm/min. Biaxial strength (σ_{bi}), in MPa, was calculated according to the following formulas:

$$\sigma_{bi} = \frac{-0.2387P(X - Y)}{h^2}$$

$$X = (1 + \nu) \ln\left(\frac{r_2}{r_3}\right)^2 + \left[\frac{1 - \nu}{2}\right] \left(\frac{r_2}{r_3}\right)^2$$

$$Y = (1 + \nu) \left[1 + \ln\left(\frac{r_1}{r_3}\right)^2\right] + (1 - \nu) \left(\frac{r_1}{r_3}\right)^2$$

where P is the failure load (in Newtons), h is the thickness of the specimen (in mm), ν is Poisson's ratio (0.3 for both composites),¹⁹ r_1 is the radius of the supporting circumference (5 mm), r_2 is the radius of the loading piston (0.6 mm), and r_3 is the specimen's radius (in mm).

Statistical analysis

After being tested for normality (Anderson-Darling test) and homogeneity of variance (Levene's test), the data were subjected to two-way ANOVA (composite and immersion period as the main variables). Multiple comparisons were performed using the Tukey test. Pearson's test was used to determine the existence of statistically significant correlations between flexural strength and mass gain after water immersion. In all cases, a global significance level of 0.05 was adopted.

RESULTS

Mass gain after water immersion

Means and standard deviations for mass gain are displayed in Table 2. The interaction and the "composite" factor were not statistically significant ($p = 0.145$ and $p = 0.144$, respectively), indicating that the mass increase resulting from water immersion was similar for both composites for a given immersion period. Up to seven days, no significant variation in mass was observed for any of the composites. Statistically significant increases in mass were observed between seven and 30 days for Filtek Silorane, and between 30 and 60 days for both composites ($p < 0.001$).

Biaxial flexural strength

The results for biaxial flexural strength are displayed in Table 2. Strength decreased significantly with time ($p < 0.001$), and no statistically significant differences were found between materials at any given immersion time. Filtek Z250 presented an approximate 56% decrease in strength after 60 days. The first statistically significant reduction in strength was observed between one and seven days of immersion. Between seven and 30 days, strength decreased, but the variation was not statistically significant. Between 30 and 60 days, the reduction in strength became statistically significant. The decrease in strength after 60 days for Filtek Silorane was approximately 46%, though the values remained fairly stable up to 30 days. Only between

Table 2 | Means and standard deviations for mass gain (in %) and biaxial flexural strength (in MPa).

Similar upper-case letters in the same column indicate statistically similar values. For any given immersion period, no statistically significant differences in mass gain or strength were detected between both materials ($p > 0.05$).

Immersion time (days)	Filtek Z250		Filtek Silorane	
	Mass gain (%)	Biaxial strength (MPa)	Mass gain (%)	Biaxial strength (MPa)
1	0.21 (0.22) C	81.7 (11.2) A	0.27 (0.29) C	70.8 (17.4) A
2	0.28 (0.25) C	68.6 (9.2) AB	0.39 (0.31) BC	63.4 (9.5) A
5	0.36 (0.20) BC	69.0 (8.5) AB	0.29 (0.27) BC	68.5 (10.1) A
7	0.38 (0.18) BC	63.3 (6.2) BC	0.25 (0.23) C	60.0 (14.8) A
30	0.70 (0.32) B	53.6 (7.6) C	0.64 (0.26) B	63.1 (8.4) A
60	1.45 (0.34) A	36.1 (4.2) D	1.11 (0.33) A	38.4 (10.1) B

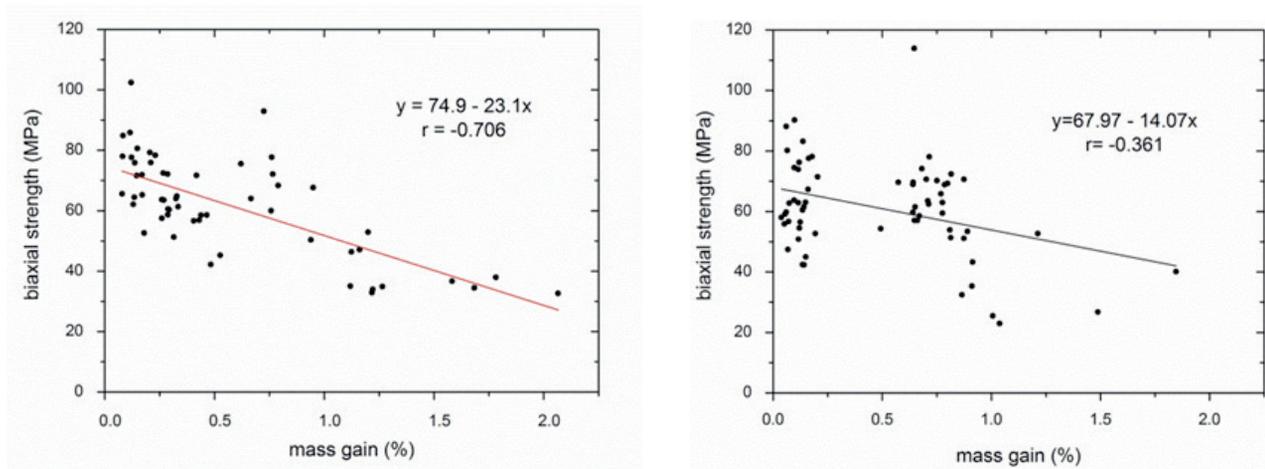


Figure 1 | Pearson's correlation test between biaxial flexural strength and mass gain due to water immersion (left: Filtek Z250; right: Filtek Silorane).

30 and 60 days, a statistically significant reduction in strength was observed.

Correlation analysis

For both composites, statistically significant correlations were found between biaxial strength and mass gain, indicating that the higher the mass gain, the lower the composite's strength (Figure 1). Pearson's correlation coefficient was higher for Filtek Z250 ($r = -0.706$, $p < 0.001$) than for Filtek Silorane ($r = -0.361$, $p < 0.01$).

DISCUSSION

The present study aimed at correlating water uptake with the reduction in strength caused by hydrolytic degradation of two commercial composites. Statistically significant correlations were found between biaxial flexural strength and mass gain after water immersion; therefore, the null hypothesis can be rejected. The experimental design did not include the assessment of the "true" water sorption, since the desorption stage described in the ISO 4049¹⁶ specification was not performed. Consequently, the variation in mass recorded at each immersion period was the result of the water uptake offset by the leaching of non-reacted monomers and oligomers.

Considering that specimens were immersed after 30 days of dry storage (i.e., fully cured) and assuming that the majority of the eluted species are released in the first 24 hours of immersion,³ it is licit to assume that the change in mass after day one reflects predominantly the water uptake.

At a given immersion period, the two tested materials presented similar mass gains, even though they differ both in their organic and inorganic content. While Filtek Z250 contains dimethacrylate monomers and zirconia/silica glass fillers, Filtek Silorane contains silorane monomers (a combination of a siloxane core and oxirane reactive groups) and quartz filler. Previous studies reported lower water sorption and solubility for Filtek Silorane in comparison to Filtek Z250.^{20,21} Also, the diffusion coefficients at early stages of water uptake for both Filtek Z250 and Filtek Silorane were calculated as, respectively, $4.10 \times 10^{-13} \text{ m}^2/\text{s}$ and $2.17 \times 10^{-13} \text{ m}^2/\text{s}$.²⁰ Such behavior is mainly attributed to the hydrophobic siloxane backbone of the silorane polymer.²² Based on the above, it can be speculated that the similar mass gain recorded for both materials is the result of a relatively high water uptake associated with a high solubility for Filtek Z250, while for Filtek Silorane the water uptake was lower, but so was elution.

Overall, the statistically similar strength values found for both materials agree with those found in previous studies.^{11,20,21,23} Between one and 60 days, the reduction in strength was slightly higher for Filtek Z250 (56%) compared to Filtek Silorane (46%). However, the two tested composites presented different behaviors, with the methacrylate-based material, Filtek Z250, showing a gradual reduction in strength, while for the silorane a statistically significant reduction in strength was observed only between 30 and 60 days. In the correlation analysis, this non-gradual decrease in strength explains the low correlation coefficient found for Filtek Silorane ($r = -0.361$).

Though correlation analysis does not imply a direct “cause and effect” relationship, it has been established in previous studies that hydrolysis of the resin matrix and the resin-filler interphase are the main mechanisms of composite degradation.^{6,7} Aging studies show different results in terms of the effect of prolonged water immersion on strength. While in some cases the immersion for periods varying between 30 days to three months did not cause significant reductions in strength,^{11,20} other authors found statistically significant reductions in mechanical properties after 30 days²⁴ and six months aging in water.⁶ Though such discrepancies can be ascribed to a different choice of materials,¹³ most of the above-mentioned studies included Filtek Silorane among the tested materials. In this case, the discrepancy may be explained by the mechanical property evaluated and choice of testing methods and specimen dimensions. Frac-

ture strength of composites is usually evaluated by flexural testing. The surface-to-volume ratios of bar-shaped specimens recommended by the ISO 4049 standard ($25 \times 2 \times 2$ mm) for uniaxial flexural testing and disc-shaped specimens (15×1 mm) are similar, approximately 2.1 mm^{-1} . Therefore, in theory, both would saturate in water at similar rates. However, stress distribution in both tests is quite different and the uniaxial specimen displays a more heterogeneous flaw population, with more diverse fracture origins (i.e., the type of flaw that originates the fracture), in comparison to the biaxial test.¹⁷ Therefore, the interaction of such flaw population with water may have different outcomes in terms of strength. Finally, the immersion medium also seems to be a factor of interest, as nine months of immersion in artificial saliva did not significantly affect mass gain or the flexural properties of a commercial composite.¹⁵

In conclusion, the findings of the present study revealed the existence of statistically significant correlations between mass gain due to water uptake and a reduction in strength for two restorative composites, with different organic and inorganic compositions. This linear relationship was shown to be material-dependent, and was stronger for the dimethacrylate-based material (Filtek Z250) in comparison to the silorane-based composite (Filtek Silorane).

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