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## Sorption, solubility, shrinkage and mechanical properties of “low-shrinkage” commercial resin composites

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### ABSTRACT

**Objective.** This study determined the volumetric shrinkage, degree of conversion, sorption, solubility, and flexure properties (before and after aging) of commercial dental composites identified as “low shrinkage”.

**Methods.** Six Bis-GMA-based composites (Point 4, ELS, Filtek Supreme, Aelite LS Posterior, Filtek Z250 and Heliomolar), a silorane-based (Filtek LS) and a dimer dicarbamate dimethacrylate-based composite (N'Durance) were studied. Total shrinkage was measured in a mercury dilatometer ( $n=3$ ). Elastic modulus and flexural strength was determined by the three point bending test before and after 4 months aging in 75% ethanol solution ( $n=10$ ). Sorption and solubility in water was assessed according to ISO 4049. Additionally, composite degree of conversion was determined using near-IR spectroscopy ( $n=3$ ). Data were analysed using one-way/two-way ANOVA or Kruskal–Wallis, and Tukey's test. Student's t-test was used to compare storage periods ( $\alpha=0.05$ ).

**Results.** The volumetric shrinkage values ranged between 1.5% (Filtek LS) and 3.4% (Point 4). The materials presented different behaviors regarding aging in ethanol, as evidenced by the large range in values of percentage reduction for elastic modulus (26–75%) and flexural strength (25–86%). Sorption values ranged from  $8.2 \mu\text{g}/\text{mm}^3$  (Aelite LS Posterior) to  $38.2 \mu\text{g}/\text{mm}^3$  (Point 4). Solubility values ranged from  $-1.5 \mu\text{g}/\text{mm}^3$  (Filtek LS) to  $5.7 \mu\text{g}/\text{mm}^3$  (Aelite LS Posterior). The degree of conversion values at 10 min ranged between 28% (Filtek LS) and 73% (Point 4). At 72 h after curing the values ranged between 39% (Filtek LS) and 83% (Point 4).

**Significance.** Among the materials identified by their manufacturers as “low shrinkage”, only Filtek LS presented statistically lower values of shrinkage compared to composites based on conventional dimethacrylates, but lower degree of conversion as well. Overall materials with higher filler content presented higher initial values of flexural properties. However, their resistance to ethanol degradation seems to be influenced by different compositional factors and, therefore, cannot be directly related to water sorption results.

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## 1. Introduction

The longevity of posterior composite restorations remains a matter of concern among clinicians. Surveys revealed that composite restorations placed in premolars and molars need to be replaced after 5–6 years, with bulk fracture and secondary caries as the main reasons cited [1–3]. The need for more durable restorations is one of the driving forces for the development of new materials and, though not always suitable for predicting clinical outcomes, laboratory evaluations are often used to estimate their potential by comparison with already established commercial products [4].

Dental composites undergo shrinkage during polymerization, which associated with the increase in stiffness of the forming polymer network, generates stresses at the interface between the tooth and the restoration, potentially increasing the risk of premature failure [5]. Recently, some dental composite materials have been developed and marketed as “low shrinkage”. Some of these materials still use Bis-GMA as the base monomer, but resort to greater filler loadings or absence of low molecular weight diluents to achieve lower shrinkage. The introduction of pre-polymerized resin filler is another attempt to reduce the shrinkage. Other approaches include the use of high molecular weight monomers, such as the methacrylate derivatives of dimer acid. In composites containing such components, the reduction in polymerization shrinkage is claimed to be due to not only the higher molecular weight of the monomer, but also to the formation of a heterogeneous network during polymerization, using a mechanism known as polymerization induced phase-separation. Nano-sized domain structures are formed at different rates, which allow viscous flow and shrinkage accommodation within the bulk of the material [6,7]. This is claimed to reduce polymerization stress, in spite of the higher conversion achieved by this material which is attributed to its more chemically reactive components.

Other alternative monomers have been proposed with epoxide ring-opening polymerization type chemistries [8], which are known to lead to lower shrinkage than free-radical, vinyl polymerizations. One commercial example is a silorane-based composite, which polymerizes via a cationic mechanism virtually insensitive to oxygen inhibition. Additionally, the presence of the siloxane core (to which the oxirane rings are attached) makes the molecule fairly hydrophobic [8–10].

Most *in vitro* studies focus on immediate mechanical properties, evaluated under dry conditions or after short-term storage in water. However, materials degradation by oral fluids and bacteria have a significant impact on physical [11–15], biological [16,17], and chemical properties [18]. Mechanical properties of conventional methacrylates used as dental composites have already been extensively explored [19], but there are still gaps of information where the newest composites are concerned. This study determined the volumetric shrinkage, flexure properties before and after aging, sorption and solubility of commercial dental composites identified as “low shrinkage”. Additionally, degree of conversion of the materials was also obtained. The null hypothesis was that low shrinkage and conventional composites would present similar

performance regarding volumetric shrinkage, mechanical properties (before and after aging), and water sorption/solubility.

## 2. Methods and materials

Eight commercial composites, all shade A3, were studied (Table 1). Six were Bis-GMA-based: a nanofilled (Filtek Supreme), a highly filled (Aelite LS Posterior), and one that does not contain low molecular weight diluent (ELS). Two composites used alternative monomers: N'Durance contains a dimer dicarbamate dimethacrylate and Filtek LS is silorane-based. Aelite LS Posterior, ELS, N'Durance and Filtek LS are considered low-shrinkage composites by their respective manufacturers.

### 2.1. Total volumetric shrinkage measurement

Total shrinkage was measured in a mercury dilatometer (ADA Health Foundation, Gaithersburg, MD, USA). Approximately 0.1 g of composite was placed on a sandblasted and silanized glass slide. A glass column was clamped to the glass slide, filled with mercury and a LVDT probe (linear variable differential transducer) was placed on top of the mercury. The composite was light cured through the glass slide, with a radiant exposure of  $18\text{ J/cm}^2$  ( $340\text{ mW/cm}^2 \times 53\text{ s}$ ), using a QTH curing unit (QHL 75 – Dentsply, Konstanz, Germany). Volumetric shrinkage ( $n=3$ ) was monitored for 60 min after the photoactivation, and the data recorded by the probe was used to calculate the volumetric shrinkage using previously measured mass and density values.

### 2.2. Degree of conversion

Degree of conversion ( $n=3$ ) was determined using near-IR spectroscopy (Vertex 70, Bruker Optik, Germany). Disc-shaped specimens were made using a silicon mold ( $h=0.8\text{ mm}$ ,  $\varnothing=7.0\text{ mm}$ ) placed between two glass slides. FTIR spectra were recorded before, at 10 min, and 72 h after photoactivation, and recorded with two scans at a resolution of  $6\text{ cm}^{-1}$ . The composite was light-cured with a radiant exposure of  $18\text{ J/cm}^2$  ( $570\text{ mW/cm}^2$ ), using a QTH unit (VIP-Bisco, Schaumburg, IL, USA). Conversion was determined by assessing the variation in peak area of the absorbance intensity at  $6165\text{ cm}^{-1}$  for methacrylate based materials [20], and at  $4155\text{ cm}^{-1}$  for silorane based material [21], in relation to the uncured material.

### 2.3. Elastic modulus and flexural strength determination

For each composite, 20 specimens were made using a split steel mold ( $10\text{ mm} \times 2\text{ mm} \times 1\text{ mm}$ ). Photoactivation was performed using a QTH unit (VIP-Bisco) and a radiant exposure of  $18\text{ J/cm}^2$  ( $570\text{ mW/cm}^2 \times 32\text{ s}$ ). The light guide tip has 11 mm in diameter, that cover the entire specimen. Half of the specimens ( $n=10$ ) were stored dry at  $37^\circ\text{C}$  for 24 h. The other half were stored in a 75% ethanol/water solution at  $37^\circ\text{C}$  for 4 months. The solution was changed weekly. The three point bending test was performed using a universal testing machine

**Table 1 – Composites tested in the study (information provided by the respective manufacturers).**

Material	Filler content (vol%)	Filler size ( $\mu\text{m}$ )	Monomers	Manufacturer
Point 4	59%	0.4	Exact composition not informed by manufacturer	SDS Kerr, Orange, CA, EUA
N'Durance	65%	0.04–0.5	Dimer Dicarbamate Dimethacrylate (DADMA), Bis-EMA, UDMA	Septodont, Louisville, CO, USA
ELS	50%	0.07–2.6	Bis-GMA, Bis-EMA	Saremco, Rohnacker, Switzerland
Filtek Supreme	57%	0.08–1.4	Bis-GMA, Bis-EMA, UDMA, TEGDMA	3M ESPE St Paul, EUA
Aelite LS Posterior	74%	0.06	Bis-GMA, Bis-EMA, TEGDMA	Bisco, Schamburg, IL, EUA
Filtek Z250	60%	0.19–3.3	Bis-GMA, Bis-EMA, UDMA, TEGDMA	3M ESPE St Paul, EUA
Heliomolar	46%	0.04–0.2	Bis-GMA, UDMA, D <sub>3</sub> MA	Ivoclar Vivadent, Schaan, Liechtenstein
Filtek LS	55%	0.05–5.0	Silorane	3M ESPE St Paul, EUA

(Instron 5565, Canton, MA, USA), with 8 mm distance between supports and cross-head speed of 0.5 mm/min. Based on the linear portion of the load vs displacement curve, flexural modulus was calculated according to Eq. (1):

$$E = \frac{C \times L^3}{4 \times b \times h^3 \times d} \times 10^{-3} \quad (1)$$

where  $E$  is the flexural modulus (GPa),  $C$  is the load recorded (N),  $L$  is the span between the supports (mm),  $b$  is the width of the specimen (mm),  $h$  is the height of the specimen (mm) and  $d$  is the deflection (mm) corresponding to  $C$ .

Flexural strength was calculated according to Eq. (2):

$$\sigma = \frac{3 \times F \times L}{2 \times b \times h^2} \quad (2)$$

where  $\sigma$  is the flexural strength (MPa),  $F$  is the maximum load recorded before the specimen fractured (N),  $L$  is the span between the supports (mm),  $b$  is the width of the specimen (mm), and  $h$  is the height of the specimen (mm).

#### 2.4. Water sorption and solubility

Disk-shaped specimens, 15 mm diameter and 1 mm thick, were made using a steel mold ( $n=5$ ). The photoactivation was performed with a radiant exposure of 18 J/cm<sup>2</sup> (900 mW/cm<sup>2</sup>  $\times$  20 s, Flash Lite 1401, Discus Dental, Culver City, CA, USA). Aiming to cover the entire specimen, the light guide was placed 10 mm from the specimen, and the irradiance was measured at this distance to calculate the real radiant exposure. After removal of the specimen from the mold, the opposite surface also received the same radiant exposure to ensure maximum curing of the specimen. The specimens were kept in a vacuum desiccator at 37 °C for 28 days. The specimens were then weighed using an analytical balance (Ohaus-Adventure, AR214N, Shanghai, China) to obtain  $m_1$ . The diameter and height of each specimen were measured to calculate the volume.

Then the specimens were immersed in distilled water at 37 °C, changed weekly to avoid alteration of the pH, for 28 days. The specimens were gently dried with absorbent paper

and weighed again to obtain  $m_2$ . The specimens then were returned to the desiccator under vacuum for 90 days, and weighed to obtain  $m_3$ . Sorption and solubility were calculated for each specimen according to Eqs. (3) and (4) (ISO 4049):

$$WS = \frac{m_2 - m_3}{V} \quad (3)$$

$$SL = \frac{m_2 - m_3}{V} \quad (4)$$

where  $WS$  is the water sorption,  $SL$  is the solubility,  $m_1$  is the mass obtained after the initial drying of the specimen ( $\mu\text{g}$ ),  $m_2$  the mass after the period of immersion in water ( $\mu\text{g}$ ),  $m_3$  the final mass after drying the specimen ( $\mu\text{g}$ ), and  $V$  is the initial volume of each specimen (mm<sup>3</sup>).

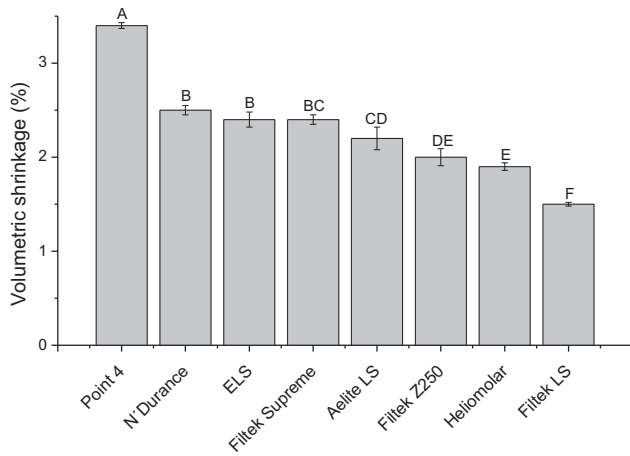
#### 2.5. Statistical analysis

Data from volumetric shrinkage, sorption and solubility were analyzed using one-way ANOVA and Tukey's test, and degree of conversion using two-way ANOVA and Tukey's test. The exception was the data from elastic modulus and flexural strength after four months that did not present homoscedasticity, and were analyzed using the non-parametric Kruskal–Wallis test. The Student's t-test was used to compare differences between the storage periods for elastic modulus and flexural strength. The global significance level adopted for all tests was  $\alpha = 0.05$ .

### 3. Results

The volumetric shrinkage values ranged between 1.5% (Filtek LS) and 3.4% (Point 4) (Fig. 1). The volumetric shrinkage of three of the materials identified as "low shrinkage" (Aelite LS Posterior, ELS, and N'Durance) did not show lower values than the other composites, but the fourth, Filtek LS was significantly lower.

The degree of conversion values at 10 min after photocuring ranged between 28% (Filtek LS) and 73% (Point 4), and after 72 h the values ranged between 39% (Filtek LS) and 83% (Point

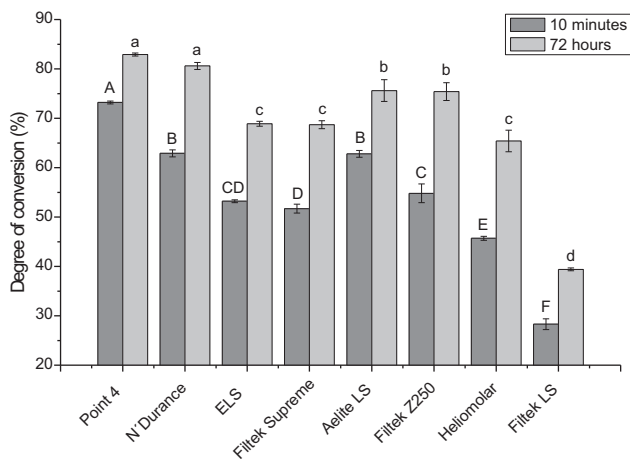


**Fig. 1 – Mean and standard deviations for volumetric shrinkage (%) determined 60 min after photoactivation. Values followed by the same letter are statistically similar ( $p > 0.05$ ).**

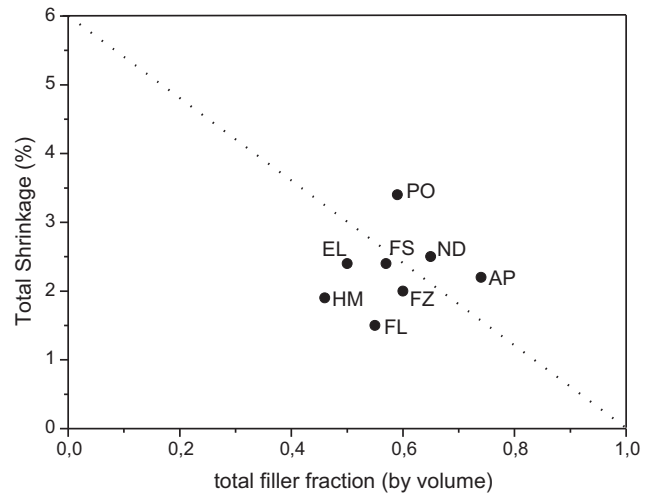
4) (Fig. 2). The degree of conversion was higher as expected at 72 h than at 10 min for all composites.

The values of elastic modulus 24 h after photoactivation and after 4 months storage in ethanol are presented in Table 2. The materials presented quite different behavior regarding aging in ethanol, as evidenced by the large range in values of percentage reduction, between 26 and 75% for elastic modulus and 25–86% for flexural strength.

Lower values for sorption were observed for Aelite LS Posterior ( $8.2 \mu\text{g}/\text{mm}^3$ ) and Filtek LS ( $12.6 \mu\text{g}/\text{mm}^3$ ), while Filtek Supreme presented the highest sorption value ( $38.2 \mu\text{g}/\text{mm}^3$ ) (Table 3). Point 4 had the lowest value of solubility ( $1.5 \mu\text{g}/\text{mm}^3$ ), but was statistically similar to that of Filtek Z250 ( $1.9 \mu\text{g}/\text{mm}^3$ ) (Table 3). N'Durance and Filtek LS presented negative values of solubility, indicating that the water was not completely removed during dry storage. Aelite LS Posterior and Heliomolar presented the highest values of solubility (5.7 and  $5.2 \mu\text{g}/\text{mm}^3$  respectively).



**Fig. 2 – Mean and standard deviations for conversion (%) determined 10 min and 72 h after photoactivation. Values followed by the same letter are statistically similar ( $p > 0.05$ ).**



**Fig. 3 – Scatter plot of total shrinkage (%) and total filler fraction (by volume). The dotted line represents the rule of mixtures (Voigt model). PO: Point 4; ND: N'Durance; EL: ELS; FS: Filtek Supreme; AP: Aelite LS Posterior; FZ: Filtek Z250; HM: Heliomolar; FS: Filtek LS.**

Fig. 3 shows a scatter plot of total shrinkage vs. total filler fraction. The dotted line represents the behavior expected based on the rule of mixtures (Voigt model), with the highest value of shrinkage of the unfilled resin being estimated as 6% based on the total volumetric shrinkage reported for a 1.5 Bis-GMA:1 TEGDMA blend [22]. Point 4 and Aelite LS Posterior presented higher shrinkage than the predicted by the rule of mixtures based on the respective filler contents, while ELS, Heliomolar and Filtek LS presented shrinkage lower than the predicted. Shrinkage values recorded for Filtek Supreme, Filtek Z250 and N'Durance were close to the values predicted by the Voigt model, which takes into account the shrinkage by reacted functional group (or the molar shrinkage coefficient) [23].

#### 4. Discussion

Several factors are influential in determining the volumetric shrinkage developed by resin composites, including the extent of polymerization, the monomer functionality and size, and the filler type and amount. Despite being reported to be

**Table 3 – Mean and standard deviations for sorption and solubility ( $\mu\text{g}/\text{mm}^3$ ). Values followed by the same letter on the same column are statistically similar (5%).**

Composite	Sorption ( $\mu\text{g}/\text{mm}^3$ )	Solubility ( $\mu\text{g}/\text{mm}^3$ )
Point 4	25.1 (6.0) <sup>B</sup>	1.5 (0.3) <sup>D</sup>
N'Durance	18.0 (0.9) <sup>CD</sup>	-0.4 (0.2) <sup>E</sup>
ELS	16.3 (3.1) <sup>D</sup>	4.0 (1.0) <sup>B</sup>
Filtek Supreme	38.2 (1.8) <sup>A</sup>	2.9 (0.6) <sup>C</sup>
Aelite LS Posterior	8.2 (1.3) <sup>E</sup>	5.7 (0.4) <sup>A</sup>
Filtek Z250	28.3 (3.3) <sup>B</sup>	1.9 (0.4) <sup>CD</sup>
Heliomolar	22.9 (0.9) <sup>BC</sup>	5.2 (0.3) <sup>A</sup>
Filtek LS	12.6 (3.5) <sup>DE</sup>	-1.5 (0.4) <sup>F</sup>

**Table 2 – Mean and standard deviations for flexural modulus (GPa) and strength (MPa) 24 h after photoactivation and after 4 months storage in ethanol. Values followed by the same letter on the same column are statistically similar (5%).**

Composite	Flexural modulus (GPa)			Flexural strength (MPa)		
	24 h	4 months	Reduction (%)	24 h	4 months	Reduction (%)
Point 4	8.5 (0.9) <sup>CD</sup>	4.8 (0.8) <sup>B</sup>	44	147.3 (23.1) <sup>BC</sup>	48.9 (5.0) <sup>C</sup>	67
N'Durance	8.4 (1.0) <sup>CD</sup>	4.1 (0.4) <sup>CD</sup>	51	100.7 (23.3) <sup>E</sup>	26.9 (5.3) <sup>E</sup>	73
ELS	6.6 (0.9) <sup>E</sup>	4.9 (0.9) <sup>B</sup>	26	138.3 (18.9) <sup>CD</sup>	103.3 (8.1) <sup>A</sup>	25
Filtek Supreme	11.9 (1.2) <sup>B</sup>	4.6 (0.7) <sup>BC</sup>	61	171.2 (23.3) <sup>AB</sup>	34.2 (5.6) <sup>D</sup>	80
Aelite LS Posterior	15.0 (2.3) <sup>A</sup>	9.1 (1.2) <sup>A</sup>	39	169.2 (26.5) <sup>ABC</sup>	64.4 (6.8) <sup>B</sup>	62
Filtek Z250	12.3 (0.9) <sup>B</sup>	3.9 (0.5) <sup>D</sup>	68	180.9 (22.8) <sup>A</sup>	32.3 (7.6) <sup>D</sup>	82
Heliomolar	6.7 (1.2) <sup>DE</sup>	1.7 (0.2) <sup>E</sup>	75	96.0 (16.7) <sup>E</sup>	19.8 (2.2) <sup>F</sup>	79
Filtek LS	9.1 (1.3) <sup>C</sup>	2.4 (0.3) <sup>E</sup>	74	111.0 (27.5) <sup>DE</sup>	15.4 (2.1) <sup>G</sup>	86

the most heavily filled composite, Aelite LS Posterior showed similar shrinkage values compared to the other microhybrids (Filtek Supreme and Filtek Z250). A possible explanation for that is that Aelite LS presents a high content of diluent monomer, which would be necessary to incorporate the high filler content. This hypothesis is reinforced by its location above the rule of mixture curve (Fig. 3).

Differences in conversion may also help explain the ranking of the materials with the intermediate filler level (50–60 vol%). Because of the close relation between conversion and shrinkage [23,24], all parameters that contribute to reactivity and network formation will also affect shrinkage. Though direct correlations cannot be drawn confidently when comparing commercial materials with non-controlled variations in monomer content, composites richer in highly reactive, more flexible monomers (such as triethylene glycol dimethacrylate and dimer acid derivatives) are expected to present higher conversion and therefore higher shrinkage. For example, Heliomolar presents the second lowest shrinkage due to a low conversion of 45.7%, which is statistically lower than the other methacrylate derivatives. In addition the pre-polymerized resin filler would contribute to its lower shrinkage. On the other hand, Point 4 presented the highest shrinkage value, in spite of the moderately high filler content (59% volume), which can be attributed to its high conversion. Besides its high conversion, Point 4 also presented a higher shrinkage than expected based on the rule of mixtures (Fig. 3), again demonstrating that increasing the filler content by itself was not sufficient to reduce the overall shrinkage of the composite.

As for the silorane-based material, conversion measurements were taken based on an absorption band in near-IR, which has been empirically correlated to the epoxy conversion [21]. The very low conversion value reported here for that material (about 30%) may have contributed to its low shrinkage. Apart from that, it has been well established that the shrinkage coefficient (change in molar volume as a function of polymerization) of epoxies (13 mol/cm<sup>3</sup>) is much lower than that observed for methacrylates (22 mol/cm<sup>3</sup>) [23]. That means upon polymerization, the number of monomer units occupying the space originally available is greater for methacrylates, i.e., more space is lost between monomers, and a greater shrinkage is observed, for a given level of conversion [23]. Also, a correlation is expected between monomer functionality and shrinkage of materials [23], based on the decreased reactivity of multi-functional species after the first group engages in

network formation [23]. Because of the tetrafunctionality of silorane molecules, relatively low conversion values were not unexpected. For N'Durance, despite the much higher molecular weight monomer in its composition, the shrinkage values were similar to those observed for the other hybrid materials containing relatively smaller monomers (2.5%). This apparent contradiction can be explained by the high reactivity and conversion produced by the combination of BisEMA, UDMA, and DADMA [25].

The greater mechanical properties observed for Aelite LS Posterior, Filtek Supreme and Filtek Z250 are probably due to the high inorganic content in these composites, in combination with an organic phase composed of monomers with stiffer backbones, which are also capable of strong intermolecular interactions [26]. On the other hand, the low inorganic content of Heliomolar and ELS, on top of their aforementioned low conversion, explain their lower mechanical properties [27,28]. For N'Durance, the high conversion was probably not sufficient to compensate for the absence of strong hydrogen bonding or for the high flexibility of the long aliphatic chain present in the dimer acid derived molecule [7], which explains the intermediate to low mechanical properties obtained. When Filtek LS is compared to Filtek Supreme, the former presented inferior mechanical performance. This can be speculated to be related to the intrinsically lower conversion of the tetra-functional silorane monomer. This increases the free volume somewhat [22], and contributes to looser networks, which can be confirmed by the severe reduction of flexure properties obtained after immersion in ethanol.

As expected, all composites showed a decrease in properties after the storage period in ethanol. This decrease is likely due to the degradation of the organic matrix [29,30], as well as the degradation of the ester linkage in the silane agent [31,32]. Heliomolar presented the greatest reduction in elastic modulus (75%), which can be attributed to its lower filler content that results in more organic matrix susceptible to degradation by ethanol. Following Heliomolar, were Filtek LS (74%), Filtek Z250 (68%) and Filtek Supreme (61%). Filtek Z250 and Filtek Supreme present low-viscosity, high molecular weight monomers (BisEMA and UDMA) as a strategy to reduce the TEGDMA content and, therefore, reduce shrinkage. However, large molecules are not as efficient crosslinkers as smaller molecules, and a less dense polymer network is likely to form when they are included, facilitating solvent penetration. In fact, both materials ranked high for water sorption. In the case of Filtek LS, as already mentioned, the pendant functional groups from the

network contribute greater free volume (due to more degrees of freedom on the chain end) and may potentiate the action of the solvent, even though its penetration tends to be suppressed by the hydrophobic character of the silorane molecule, as evidenced by its low water sorption.

N'Durance and Point 4 presented intermediate modulus reduction values, and ELS and Aelite LS Posterior were the most stable against ethanol degradation. ELS's resistance to ethanol degradation may be attributed to its low water sorption, which is a result of the absence of more hydrophilic monomers, such as TEGDMA and UDMA. In the case of Aelite LS Posterior, the high filler loading might have minimized the sorption of solvent (to be discussed in detail later), thus leading to smaller reductions in the mechanical properties.

In regards to sorption and solubility, all composites passed the requirements set forth in the ISO 4049, i.e., sorption was below  $40 \mu\text{g}/\text{mm}^3$  and solubility below  $7.5 \mu\text{g}/\text{mm}^3$ . Filtek Supreme presented the highest sorption value, followed by Filtek Z250, Point 4 and Heliomolar. For Filtek Supreme, Filtek Z250 and Point 4 the presence of TEGDMA as a diluent may contribute to the increased sorption because of the hydrophilicity of this monomer. For Heliomolar, in spite of the lower overall filler volume fraction, the small size of particles leads to enhanced filler/matrix surface interactions. In the next range of sorption, ELS, N'Durance and Filtek LS presented lower sorption values, in this case more likely due to the presence of more hydrophobic monomers. The lowest sorption value was achieved by Aelite LS Posterior, which can be explained by two synergistic factors: the higher filler content (and thus lower organic content) [33], and the greater hydrophobicity of the organic phase (mostly BisEMA in place of BisGMA) [34].

The results of solubility are expected to be correlated with the water sorption, since the solvent needs to penetrate the material for unreacted components to be able to leach out. However, conversion and crosslinking density play a major role on how sorption and solubility correlate [35]. The material with the highest sorption (Filtek Supreme) presented intermediate solubility, which is probably explained by a slightly lower network density in this material. In that way, the polymer was able to swell, but there were not many unreacted monomers available to leach out. Heliomolar presented relatively high sorption and solubility, due to its low conversion, as well as the already mentioned large surface area of the silanated filler, more prone to degradation [27,28,36]. For composites in the same range of sorption of Heliomolar (Point 4 and Filtek Z250), the solubility was significantly lower. This may attributed not only to a more favorable filler/matrix ratio, but also to a higher conversion. For the most hydrophobic composites (N'Durance and Filtek LS), the lower sorption values were reflected in lower solubility values. The negative values found were most likely an artifact: the hydrophobicity of these materials made solvent transport very difficult in and out of the specimen, causing some water molecules to be trapped. For ELS and Aelite LS, in spite of a relatively low sorption, solubility values were the highest, which suggests that the degradation was more concentrated at, but not limited to, the surface of the specimen for these two materials. For ELS, the low degree of conversion can explain the solubility of the outer layers [27,28,36]. In the case of Aelite

LS Posterior, this can be attributed to the high filler content and broad filler size distribution, which contributes to more silanated interfaces for degradation. It is noteworthy that some solubility values were negative, similar to results previously reported [37]. One possible explanation is that some solvent remained entrapped in the network due to diffusivity constraints, which is indeed corroborated by the low sorption of the very hydrophobic materials (N'Durance and Filtek LS). In particular for these higher functionality monomers present in Filtek LS, the low conversion does not necessarily mean that residual monomers are free to leach, but most likely that there are many unreacted groups pendant from the network, since the reactivity of any multifunctional molecule tends to decrease as it becomes integrated within the network [23].

The null hypothesis that low shrinkage and conventional composites would present similar performance regarding the properties evaluated in this study was rejected in part. This study has shown that, among the materials identified by their manufacturers as "low shrinkage", only Filtek LS presented statistically lower values of shrinkage compared to composites based on conventional dimethacrylates. In terms of initial flexural properties, overall materials with higher filler content presented higher initial values of elastic modulus and flexural strength. However, their resistance to ethanol degradation seems to be influenced by different compositional factors and, therefore, cannot be directly related to water sorption results. The low shrinkage composites presented the lowest values of water sorption. As for solubility two of them presented negative values (N'Durance and Filtek LS), and the others presented the highest values (ELS and Aelite LS).

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