Comparative analysis of polymerization shrinkage of different resin composites

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This study sought to compare the shrinkage of 3 resin composites after polymerization, using different curing modes and 2 methods of analysis, with 45 samples in each group. To evaluate free linear shrinkage, specimens were prepared in Teflon molds (8 mm diameter x 2 mm thick) with 1 of 2 methacrylate-based resins or a silorane-based resin. To evaluate wall-to-wall shrinkage, cavities (1.5 mm thick x 3 mm diameter) were prepared in 45 healthy bovine incisors and then restored. In both tests, the same curing lights were used: conventional quartz-tungsten-halogen, a conventional light-emitting diode (LED), and an exponential LED. Gaps were measured microscopically, and the gap percentage was calculated. The results were analyzed by 2-way ANOVA and Tukey's test ($\alpha = 0.05$).

Curing modes differed significantly in the free linear shrinkage test group, while resin composites did not. In the wall-to-wall shrinkage group, there were significant differences between the resin composites.

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Resin composites have been the material of choice for the restoration of compromised dental structures and are used extensively for esthetic restorations in anterior teeth. These composites also are becoming increasingly popular in posterior teeth due to advances made in their chemical, physical, and mechanical properties. Despite their advantages, these composites have an intrinsic characteristic of shrinkage during the curing process as monomers pass from free floating molecules to rigid polymeric chains.[1] This contraction produces tensions that tend to concentrate on tooth/restoration interfaces, weakening the adhesive union and creating marginal gaps that can lead to microleakage, postoperative sensitivity, and recurrent caries.[1-3]

Adding inorganic filler particles to the matrix of the composites has significantly reduced the polymerization shrinkage and thermal expansions that were observed in previous materials. The size and shape of particles and the organic-resin matrix (which is responsible for shrinkage due to polymerization) have changed as well.[4]

These newer composite materials have been developed with the help of nanotechnology. This technology involves the production of inorganic filler for the composites. By using chemical and physical methods, filler particles of quartz, fused glass, and ceramics are transformed into nanometric particles (ranging in size from 0.1 to 100 nm).[4,5] Currently, there are 2 types of composites produced with nanotechnology: nanofilled resins, whose composition involves particles and clusters (known as *nanoclusters*); and nanohybrid resins, which combine nanofillers with small particles, similar to those found in microhybrid resins.[6] An optimal distribution of different particles of varying sizes allows an increase in the inorganic content of the composite resin, consequently leading to a potential decrease in polymerization shrinkage.[4]

In 2007, a low-shrinkage composite was introduced (Filtek Silorane, 3M ESPE), based on a system of silorane monomers, end-products of the molecular reaction between oxirane with siloxane.[7,8] This resin combined the advantages of the 2 individual components: low polymerization shrinkage due to a ring-opened system (oxirane) along with the hydrophobic characteristics of siloxane. Unlike the linear reactive groups of methacrylates—which polymerize by a radical addition reaction of double bonds—silorane-based resins polymerize through a cationic reaction of ring-opening (starting with cleavage rings), thereby gaining space and offsetting the loss of volume that occurs in the next step, while simultaneously reducing the extent of polymerization shrinkage.[8-10]

The curing mode also affects contraction due to polymerization.[10-14] The high intensity of light used in conventional techniques results in higher monomer conversion but also increases shrinkage stress.[11] A slower polymerization with a lower intensity light makes it possible to prolong the pre-gel phase, increasing the possibility of relief from contraction stress.[12,13] Variations in these methods include exponential mode, where light intensity is increased gradually (either soft start or ramp), and pulse delay (discontinuous). The discontinuous mode is performed with pulses separated by a time interval; the first pulse has a low-intensity light followed by a pulse of higher intensity light.[11,12,14,15]

This study sought to evaluate the polymerization shrinkage of 3 resin composites: 2 methacrylate-based (nanofilled and microhybrid) and 1 silorane-based (microhybrid). All 3 composites were light-cured by different curing modes in order to examine free linear shrinkage and wall-to-wall shrinkage.

Materials and methods

This study used 2 methacrylate-based resin universal composites—one nanofilled (Filtek Z350XT, 3M ESPE), one microhybrid (Filtek Z250, 3M ESPE)—and one silorane-based (microhybrid) resin composite specifically formulated for posterior restorations (Filtek P90, 3M ESPE) (Table 1).[16-18] Ninety specimens were prepared and divided into 18 groups (n = 5) according to experimental test, resin composite, and curing mode.

Composites were photocured using a quartz-tungsten halogen (QTH) lamp and a light-emitting diode (LED) (Elipar Freelight 2, 3M ESPE) employing different curing modes: conventional QTH, involving continuous exposure of 400 mW/cm^2

Table 1. Characteristics of resin composites used in this study.

Resin composite	Composition	Type (Shade)	Filler loading by weight (%)
Filtek Z350 XT	Matrix: bisphenol A glycol dimethacrylate (Bis-GMA), ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), polyethylene glycol dimethacrylate (PEGDMA); Filler: silica (4-20 nm non-aggregated), zirconia (4-11 nm, non-aggregated and aggregated), clusters of zirconia/silica	Nanofilled (A3 body)	78.5
Filtek Z250	Matrix: Bis-GMA, Bis-EMA, UDMA, TEGDMA; Filler: zirconia/silica (average 0.01-3.50 µm)	Microhybrid (A2)	78.0
Filtek P90	Matrix: silorane; Filler: quartz, radiopaque yttrium fluoride (0.1-2 µm; average 0.47 µm)	Microhybrid (A2)	76.0

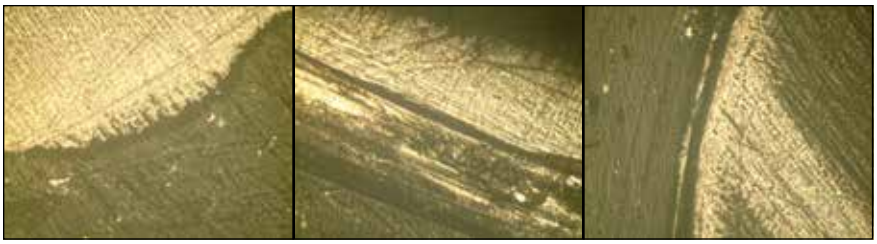

Fig. 1. Photomicrograph showing marginal gaps of free linear shrinkage for Filtek Z350 XT, Filtek Z250, and Filtek P90, using the exponential LED (magnification 100X).

Table 2. Mean percentages and standard deviation (SD) of resin composites after polymerization, based on curing method.

Resin composite	Method	Mean (SD)
Filtek Z350 XT	Quartz-tungsten-halogen (QTH)	0.96 (0.14)
	Conventional LED	0.76 (0.03)
	Exponential LED	0.73 (0.05)
Filtek Z250	QTH	0.97 (0.17)
	Conventional LED	0.82 (0.13)
	Exponential LED	0.65 (0.07)
Filtek P90	QTH	0.79 (0.16)
	Conventional LED	0.82 (0.09)
	Exponential LED	0.65 (0.16)

Table 3. Comparison of the average percentage and standard deviation (SD) for curing methods in terms of free linear shrinkage (n = 15).

Method	Average (SD)
QTH	0.91 (0.17)[a]
Conventional LED	0.80 (0.09)[a]
Exponential LED	0.68 (0.11)[b]

Different lowercase letters indicate statistically significant differences by the Tukey's test ($P < 0.05$)

for 40 seconds; conventional LED, involving continuous exposure of 900 mW/cm^2 for 20 seconds; and exponential LED for 5 seconds, followed by an exposure of 900 mW/cm^2 for 15 seconds. The light intensities of the curing bulbs were measured with QTH and LED radiometers (Demetron, Kerr Corporation) before the curing of samples from each experimental group.

Free linear shrinkage

Using a Teflon split mold (8 mm diameter x 2 mm thick), 45 specimens were made by inserting resin composite in a single increment and covering it with a polyester strip and a glass slide to promote a flat surface. All specimens were photocured; 10 minutes later, extra filling material was removed by wet polishing with 600 and 1200 grit silicon carbide papers. Next, the specimens were immersed in distilled water to remove residual material. A graphite dust was rubbed over the resin-Teflon interfaces to determine where gaps were present. Composite-mold interfaces were examined by using an automatic photomicroscope (magnification 100X). All interfacial gaps were measured (in µm) using a distance (space) scale present on the photomicroscope's screen. The percentage of linear shrinkage was calculated as a function of cavity internal length by the equation

$$X\,(\%) = G_{(\mu m)} \times 100/T_{(\mu m)}$$

where G indicates the maximum gap width (together with the opposite gap) and T indicates the Teflon length (8 mm = 8000 µm).

Wall-to-wall shrinkage

This research was approved by the Ethics Committee on Animal Research, Brazil (Protocol No. OD021/2010). This sample used 45 bovine central incisors stored in distilled water at room temperature. The roots were removed and a flat enamel surface was obtained by grinding buccal surfaces with wet silicon carbide paper (320, 600, and 1000 grit) until an area at least 6 mm in diameter was exposed. Standardized cylindrical cavities (3 mm diameter x 1.5 mm depth) were prepared using a diamond cylindrical bur in a high-speed handpiece under wet conditions. Cavity preparations were finished with a cylindrical stainless steel bur (No. 57, SS White Burs, Inc.) also under wet conditions. A new bur was used for each preparation. Cavity preparation walls were treated with phosphoric acid and adhesive systems, according to the manufacturer's instructions. Restorations with Filtek Z350 XT and Filtek Z250 used

Fig. 2. Photomicrograph showing marginal gaps of wall-to-wall shrinkage for Filtek Z350 XT, Filtek Z250, and Filtek P90, using the exponential LED (magnification 100X).

Table 4. Average percentage and mean deviation (SD) of composite resins measured in terms of wall-to-wall shrinkage (n =15).

Resin composite	Average (SD)
Filtek Z350 XT	0.37 (0.05)[b]
Filtek Z250	0.30 (0.06)[a]
Filtek P90	0.21 (0.04)[c]

Different lowercase letters indicate statistically significant differences by the Tukey's test ($P < 0.05$)

Table 5. Descriptive analysis of wall-to-wall shrinkage average percentages and standard deviation (SD) of composite resins, based on mode of photopolymerization.

Resin composite	Method	Average (SD)
Filtek Z350 XT	QTH	0.38 (0.06)
	Conventional LED	0.37 (0.05)
	Exponential LED	0.37 (0.04)
Filtek Z250	QTH	0.36 (0.04)
	Conventional LED	0.30 (0.04)
	Exponential LED	0.25 (0.05)
Filtek P90	QTH	0.21 (0.14)
	Conventional LED	0.20 (0.03)
	Exponential LED	0.21 (0.04)

the Adper Single Bond adhesive system (3M ESPE). Restorations with Filtek P90 used the Silorane Adhesive System (3M ESPE). Resin composites were inserted, covered, photocured, and stored in the same manner as samples for which free linear shrinkage were examined. To allow for a proper examination of margin gaps between dentin and restoration, excess filling material on the enamel surface was removed by using a wet polishing machine (DPU-10, Struers, Inc.) with 600- and 1200-grit silicon carbide papers. Composite-mold interfaces were examined, and all interfacial gaps were measured in the same manner as the free linear shrinkage samples. The percentage of shrinkage was calculated using the formula

$$X = Sg \times 100\%/2R$$

where Sg is the sum of the gaps (in μ) and R is the cavity radius (1.5 mm = 1500 μm).

Statistical analysis

All results were analyzed statistically using factorial ANOVA (a x b) and the parametric Tukey's test with a significance level of 5% for both tests.

Results

Free linear shrinkage

Figure 1 shows the gaps of the resins analyzed by free linear shrinkage, while Table 2 presents a descriptive analysis of mean percentages for resin composites after polymerization by the various methods. Two-way ANOVA showed differences based on photocuring methods; however, there were no significant differences between the resin composites when analyzed individually nor in composite versus method interaction. The mean percentages for free linear shrinkage were compared to individual curing methods (Table 3). Tukey's test ($P < 0.05\%$) showed that the exponential LED method had the lowest free linear shrinkage values compared to those of the other curing methods. No significant differences were found between conventional QTH or conventional LED photocuring.

Wall-to-wall shrinkage

Figure 2 presents the gaps of the resins analyzed according to wall-to-wall shrinkage. According to 2-way ANOVA, there were significant differences between the resin composites. Filtek P90 showed the lowest wall-to-wall polymerization shrinkage, followed by Filtek Z250 and Filtek Z350 XT (Table 4). The differences between the mean values of wall-to-wall shrinkage were not significant for photocuring modes, resins, or type of photocuring. A descriptive statistical analysis of resin composite photocured by different methods can be seen in Table 5. It was found that the 3 composites were different when analyzed individually without considering the curing method.

Discussion

In the present study, the polymerization shrinkage of resin composites was evaluated by 2 different methods. First analyzed in 1983 by Bowen et al, the study of free linear shrinkage involved observing the behavior of materials under conditions that allowed them to contract.[19] Teflon molds were chosen because they do not react with resin composites, allowing the composites to shrink freely in the cavities during polymerization.[4,20] The wall-to-wall shrinkage method uses an adhesive system that causes the material to shrink under restricted conditions.[21] Opposite results were obtained from the 2 methods, implying that they must be interpreted separately due to the different methodologies used to analyze contraction.

When evaluating free linear shrinkage, significant differences were seen between curing modes, while the resins did not differ. There were no substantial differences between doses applied in the curing methods, although the exponential LED generated the lowest dose, which could explain why this group had the lowest gap values.[9,12,14]

The use of adhesive systems in the evaluation of wall-to-wall shrinkage may have led to lower marginal gaps in keeping with a 2002 study by Irie et al.[20] These authors explored multiple correlations between the contraction, adhesion, and formation of marginal gaps immediately after curing, using 3 types of restorative materials (composites, compomers, and resin-modified glass ionomer); examining

marginal gaps formed in cavities made in human teeth and in cavities made in a Teflon mold; and measuring the diametric force of contraction and shear forces to enamel and dentin. Smaller marginal gaps were observed in natural teeth compared to Teflon molds, indicating the importance of adhesion between tooth and restoration to reduce polymerization shrinkage.[20] The present study also saw a reduced percentage of gaps in the bovine cavities compared to Teflon molds, regardless of methodological differences. Other variables that may have influenced wall-to-wall shrinkage include the bond strength to withstand the stresses of contraction and the modulus of elasticity inherent in each resin-based material.[4,17]

The magnitude of the contraction force depends on the balance between the forces of adhesion and contraction of the material in a cavity.[21] In keeping with previously published studies, the chemical composition of resin composites used in the present study had a greater effect on wall-to-wall shrinkage than did factors related to photocuring.[4,22] The silorane-based resin Filtek P90 showed the smallest amount of polymerization shrinkage, in keeping with the literature.[7,9,10,23-26] The silorane molecule has a siloxane chain linked to 4 oxirane rings that open during polymerization to join with other monomers.[20] Siloxanes are known for their industrial applications because of their distinct hydrophobicity, while oxirane is known for its low shrinkage and excellent stability against forces and physicochemical influences. Nanotechnology ensured that the siloxane system's initiators (camphorquinone, iodonium salt, and electron donors) and the inorganic particles provided improved the performance of the composite combined with the use of a proper adhesive system.[8] Opening the oxirane ring causes a volumetric expansion that partially offsets the contraction resulting from molecular adhesion. According to the literature, silorane-based composites show <1.0% total polymerization shrinkage compared with the 2.0%-3.5% presented by the bisphenol A glycol dimethacrylate (Bis-GMA)-based composites.[7,18] The contraction of Filtek Z250 and Filtek Z350 XT was also <1.0%.[16,17]

Ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA) and urethane dimethacrylate (UDMA)—high molecular weight monomers that decrease the number of crosslinks and reduce polymerization shrinkage—were added to the microhybrid Filtek Z250.[17] In addition to these monomers, the nanofilled resin Filtek Z350 XT also contains a small amount of the monomer polyethylene glycol dimethacrylate (PEGDMA), which helps to increase material viscosity and reduce polymerization shrinkage.[16] The inorganic content of PEGDMA also includes isolated zirconia nanoparticles approximately 4 to 11 nm in size (in previous resins, these nanoparticles were only present in conjunction with silica nanoclusters that ranged in size from 5 to 20 nm). These particles, which are now even smaller and vary more in size (due to strong sintering), may increase the amount of inorganic content in this material and decrease polymerization shrinkage.[16] Both the inorganic filler concentration and monomeric content affect polymerization stresses; however, the stronger influence of the resin matrix suggests that it may be possible to reduce stress by modifying resin composition without sacrificing filler content.[27] Wall-to-wall shrinkage values of the nanofilled Filtek Z350 XT were slightly higher than those of the microhybrid Filtek Z250. The viscosity of Filtek Z250 may have contributed to these results, since this resin has a smaller number of filler particles and is less viscous than Filtek Z350 XT, allowing it to settle in the cavity and thus decreasing polymerization shrinkage.[16,17]

Conclusion

This study concluded that all the composites showed low percentages of polymerization shrinkage, regardless of evaluation method. The exponential LED method generated the lowest percentage of shrinkage for all resins used, suggesting that polymerization modes with soft start can reduce a resin's tendency to contract. In wall-to-wall shrinkage, Filtek P90 had the lowest percentage of gaps, showing that the improved inorganic and organic matrix of this material was effective at reducing the contraction forces, thus diminishing the stress on restorations. This finding is particularly important to ensure the greater longevity of dental restorations.

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