



ELSEVIER

available at www.sciencedirect.comjournal homepage: www.intl.elsevierhealth.com/journals/dema

Alternative methods for determining shrinkage in restorative resin composites

Gabriela Queiroz de Melo Monteiro^{a,b}, Marcos Antonio Japiassú Resende Montes^{b,*},
Tiago Vieira Rolim^c, Cláudia Cristina Brainer de Oliveira Mota^d,
Bernardo de Barros Correia Kyotoku^e, Anderson Stevens Leônidas Gomes^e,
Anderson Zanardi de Freitas^f

^a Dental School, Centro Universitário de João Pessoa - UNIPÊ, João Pessoa, PB, Brazil

^b Department of Restorative Dentistry, Universidade de Pernambuco - FOP/UPE, Av. Gen Newton Cavalcanti, 1650, Camaragibe, PE 54753-220, Brazil

^c Department of Mechanical Engineering, Universidade Federal de Pernambuco - UFPE, Recife, PE, Brazil

^d Graduate Program in Dentistry, Universidade Federal de Pernambuco - UFPE, Recife, PE, Brazil

^e Department of Physics, Universidade Federal de Pernambuco - UFPE, Recife, PE, Brazil

^f Nuclear and Energy Research Institute, IPEN-CNEN/SP, São Paulo, SP, Brazil

ARTICLE INFO

Article history:

Received 30 December 2009

Received in revised form

22 August 2010

Accepted 28 April 2011

Available online xxx

Keywords:

Dental composites

Polymerization shrinkage

Siloranes

Buoyancy

Optical coherence tomography

Coordinate measuring machine

ABSTRACT

Objectives. The purpose of this study was to evaluate polymerization shrinkage of resin composites using a coordinate measuring machine, optical coherence tomography and a more widely known method, such as Archimedes Principle. Two null hypothesis were tested: (1) there are no differences between the materials tested; (2) there are no differences between the methods used for polymerization shrinkage measurements.

Methods. Polymerization shrinkage of seven resin-based dental composites (Filtek Z250TM, Filtek Z350TM, Filtek P90TM/3M ESPE, Esthet-XTM, TPH SpectrumTM/Dentsply 4 SeasonsTM, Tetric CeramTM/Ivoclar-Vivadent) was measured. For coordinate measuring machine measurements, composites were applied to a cylindrical Teflon mold (7 mm × 2 mm), polymerized and removed from the mold. The difference between the volume of the mold and the volume of the specimen was calculated as a percentage. Optical coherence tomography was also used for linear shrinkage evaluations. The thickness of the specimens was measured before and after photoactivation. Polymerization shrinkage was also measured using Archimedes Principle of buoyancy (n = 5). Statistical analysis of the data was performed with ANOVA and the Games-Howell test.

Results. The results show that polymerization shrinkage values vary with the method used. Despite numerical differences the ranking of the resins was very similar with Filtek P90 presenting the lowest shrinkage values.

Significance. Because of the variations in the results, reported values could only be used to compare materials within the same method. However, it is possible rank composites for polymerization shrinkage and to relate these data from different test methods. Independently of the method used, reduced polymerization shrinkage was found for silorane resin-based composite.

© 2011 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +55 81 31847667/99660456; fax: +55 81 31847667.

E-mail address: majrm@uol.com.br (M.A.J.R. Montes).

0109-5641/\$ – see front matter © 2011 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

doi:10.1016/j.dental.2011.04.014

1. Introduction

Despite the major developments in new restorative materials, all resin-based composites present a certain degree of volume reduction due to the polymerization reaction. Assuming that these materials are bonded to prepared dental cavities, this volume contraction will lead to internal stress generation, which in turn, compromises the mechanical and chemical stability of the restoration and may lead to the loss of marginal integrity [1]. As a consequence, marginal leakage of saliva and its components will occur resulting in post-operative sensitivity, discolored margins, recurrent caries and fractures of the restoration margins [2]. These clinical consequences are the main reasons for restoration substitution, and explain why polymerization shrinkage is recognized as the main limitation of these materials [3,4].

Many studies have been conducted to evaluate polymerization shrinkage of resin composites. The results indicate that the volume contraction is dependent on the filler concentration, polymerization characteristics, volume and cavity design, restorative procedure and light intensity used for photoactivation [2]. In addition, polymerization shrinkage has a strong influence on stress generation and most of these tensions are developed in the first few seconds after irradiance [5]. The characterization of the shrinkage behavior and the polymerization reaction itself are an important aspect in the development of new restorative materials [6].

To reduce shrinkage, the main approaches adopted so far are modifications in the filler amount, shape or surface treatment. Versatile methods to modify the monomer matrix have been developed, starting with typical dimethacrylates with a reduced reactive group. Other approaches include the development of liquid crystal monomers or ring-opening systems to produce non-shrinking or minimally shrinking dental composites that contain spiroorthocarbonates as additives to dimethacrylate or epoxy resins. A new resin system, called siloranes, claims to have combined the two key advantages of the individual components: low polymerization shrinkage due to the ring-opening oxirane monomer and increased hydrophobicity due to the presence of the siloxane species [7].

However, the magnitude of the shrinkage is dependent on the methodology used to measure it. The results obtained for any of the methods recently published also varies between operators. Therefore, comparisons between published results are quite difficult with research being carried out in different laboratories with different equipment and operators [8].

Many methods have been described to measure polymerization shrinkage: bonded disk method [9], mercury dilatometer [10], optical method [11,12], gas pycnometer [13], the use of a strain gage [8], linear displacement [10], free linear shrinkage, wall-to-wall shrinkage [14], among others. However, each method for polymerization shrinkage evaluation depends on one physical principle for measurement.

It is in this context that new polymerization shrinkage evaluation methods appear, not only to determine volume variations but mainly to enable comparisons between the results obtained for each method. This is of greater importance to assure the reproducibility and veracity of the results.

Coordinate measuring systems were developed at the end of the 20th century to fulfill the industrial sector's need for easy and quick inspections of fabricated pieces using automated manufacturing systems. The primary goal of coordinate measuring machines (CMMs) is to obtain the Cartesian coordinates of points on a solid surface [15].

A CMM is composed of four interconnected rigid parts, three mobile and one fixed base. A CMM with a fixed working table and a mobile bridge is the most common type. In this type of CMM, the object to be measured is placed on the fixed granite table and the operator dislocates each of the three mobile parts along the three axes using a joystick in the following sequence: the bridge (along the OX axes), the car (along the OY axes) and the probe column (along the OZ axes). Finally, a ruby probe touches a specific point on the object. Each part of the machine has a built-in guide rail, so that the relationship between the axes allows a point to be located in all three planes with one check. The resulting data are mathematically processed in a computerized system to provide dimensional and geometrical measurements of any kind of object with high precision [16].

Optical coherence tomography (OCT) is a non-invasive medical diagnostic imaging modality with high resolution that can give near-histologic images. The basic principle of OCT is analogous to computerized tomography (which uses X-rays), magnetic resonance imaging (which uses spin resonance), and B-scan ultrasound (which uses sound waves). Nevertheless OCT uses only light to derive its image in a non-contact, non-invasive system [17].

OCT is based on a Michelson interferometer with a low coherence, broadband light source. The light generated in an OCT system is divided in two: one part follows a sample arm containing the item of interest, and the other follows the reference arm, which is usually a mirror. Reflected light is then recombined. When the path length of light from the reference mirror is the same as the tissue or sample, an interference fringe is detected. Because the reference mirror is moved by known increments, the position of the reflected light within the sample can be determined by the optical scattering properties of tissues. These interference patterns generate a reflectivity profile, called an A-scan. A two-dimensional tomographic image can be created by combining a series of A-scans [18].

Archimedes Principle (buoyancy of a material in fluid) is a well-established test method that can be used to measure volumetric dimensional changes by measuring density variations. This principle states that a body immersed in a fluid is buoyed up by a force equal to the weight of the dispersed fluid. Whether a given body will float, sink, or remain static in a given fluid is dependent on both the weight and volume of that material. The relative density – the weight per unit volume of the body compared to that of the fluid – determines the buoyant force [1,19–21].

The determination of dimensional changes in resin composites, shrinkage or expansion, through density measurements using this principle is a relatively simple and low-cost method. It basically consists of weighing the material under study several times in two distinct environments of known density; air is conventionally used as one of environment. Several liquids such as mercury, distilled water

Table 1 – Composition, manufacturers and batch numbers of the materials studied.

Composite	Matrix ^a	Filler content; filler size; % by weight/volume	Manufacturer ^b ; batch no.
Filtek Z250™	BisGMA, UDMA and BisEMA BisGMA	Zirconia/silica; microhybrid; 82/60 [11]	
Filtek Z350™	3M/ESPE; 9EM UDMA, TEGDMA and BisEMA	Zirconia/silica and silica; nanoparticle; 78.5/59.5	3M/ESPE; 8UU
Filtek P90™	Silorane	Quartz and yttrium fluoride; microhybrid; 76/55	3M/ESPE; 9CH
4 Seasons™	BisGMA, UDMA and TEDMA	Barium glass, ytterbium trifluoride, Ba–Al-fluorosilicate glass, highly dispersed silicon dioxide and spheroid mixed oxide; nanohybrid; 75–77/55–58	Ivoclar Vivadent; 12979
Tetric Ceram™	BisGMA, UDMA and TEDMA	Barium glass, ytterbium trifluoride, Ba–Al-fluorosilicate glass, highly dispersed silicon dioxide and spheroid mixed oxide; microhybrid; 79/60	Ivoclar Vivadent; 08516
Esthet-X™	U-BisGMA, BisEMA and EGDMA	Borosilicate/aluminum/barium glass and silica; nanohybrid; 77/– [31,35]	Dentsply Caulk; 0709132
TPH Spectrum™	U-BisGMA	Borosilicate/aluminum, barium and silica; microhybrid; 77/57.1 [31]	Dentsply Brazil; 135676B

All composites were A2 color. (–) Information not available from the manufacturer.

^a BisGMA, bisphenol-glycidyl methacrylate; UDMA, urethanethyl dimethacrylate; TEGDMA, triethylene glycol dimethacrylate; BisEMA, bisphenol-polyethylene glycol dimethacrylate; U-BisGMA, urethane-modified bisphenol-glycidyl methacrylate.

^b 3M ESPE, St. Paul, MN, USA; Ivoclar Vivadent, Schaan, Liechtenstein; Dentsply Caulk, Milford, DE, USA; Dentsply Indústria e Comércio Ltda, Petrópolis, RJ, Brazil.

and silicone oil can be used as the second surrounding medium.

The purpose of this study was to evaluate shrinkage of resin composite polymerization using CMM, OCT, and a more widely known method, such as Archimedes Principle. Two null hypotheses were tested: (1) there are no differences between the materials tested; (2) there are no differences between the methods used for polymerization shrinkage measurements.

2. Materials and methods

The materials, manufacturers, composition and batch numbers for this study are listed in Table 1.

All photoactivation procedures were done using a halogen light output (Optilight Plus™, Gnatus, São Paulo, Brazil) with a 10 mm diameter light conductor. Just before each specimen preparation, light intensity was measured with an external radiometer (Gnatus, São Paulo, Brazil), always within the range of 550–600 mW/cm². The composites were photoactivated for 40s in continuous mode, which ensures a radiant exposure between 22 and 24 J/cm² and, therefore, adequate polymerization [22,23].

2.1. Coordinate measuring system

A predefined quantity (0.135 ± 0.010 g) of each test material was placed in bulk in a cylindrical Teflon mold (7 mm × 2 mm). Composites were then covered with a mylar strip and pressed with a microscope glass slide to ensure adequate adaptation into the mold. Photoactivation was performed using the

established protocol, and the specimens were then carefully removed from the mold and stored in a dark environment for 15 min ($n=5$) (Fig. 1).

A CMM (Crysta 574/Mitutoyo, Japan) with measurement uncertainty of 2.0 μm was used. To proceed with the measurements, specimens were fixed on a flat glass plate with caulking putty. Measurements were done according to the following protocol:

- (1) Teflon mold geometry determination:
 - a. 5 points on the top surface;

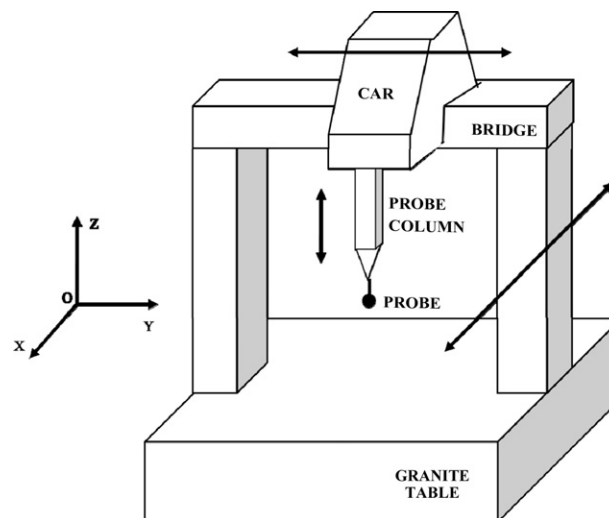


Fig. 1 – Constituent parts of a fixed working table and a mobile bridge CMM.

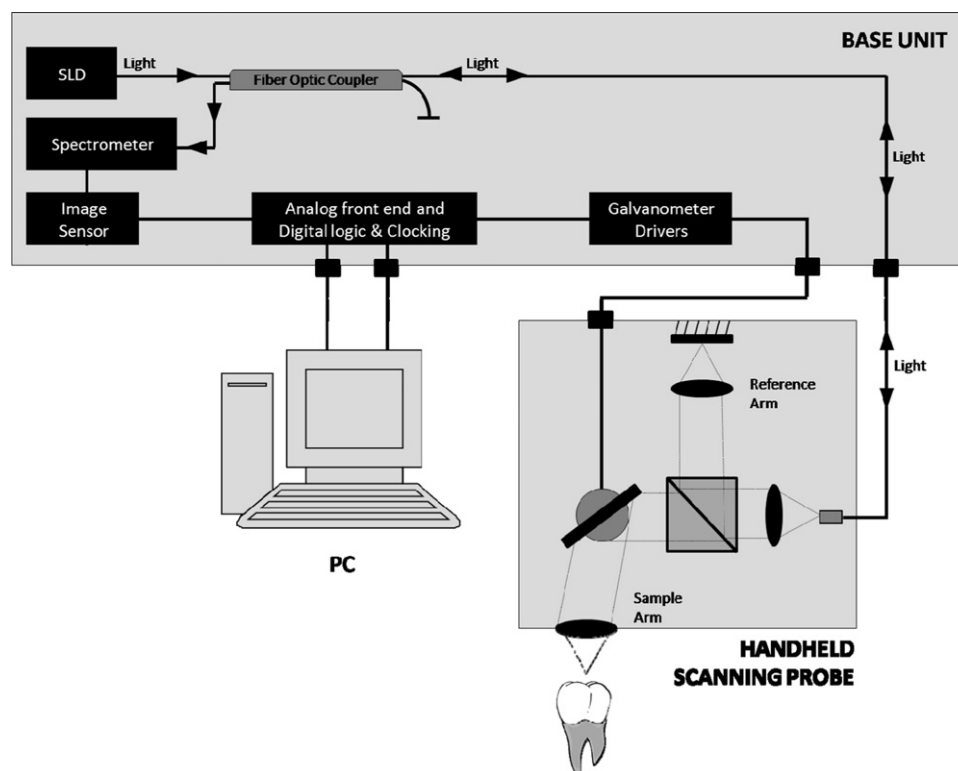


Fig. 2 – Schematic drawing of the commercial OCT SR-OCT: OCP930SR (adapted from Thorlabs, New Jersey, USA).

- b. 2 points at the bottom surface;
 - c. 4 points at the diameter.
- (2) Specimens geometry determination:
- a. Determination of the origin at the glass plate;
 - b. 4 points at the diameter;
 - c. 2 points at the top surface.

The dimensions of the Teflon mold and the specimens (diameter and height) were then used to determine their volumes according to the following equation:

$$V = \pi r^2 h$$

where V is the final volume, π is a mathematical constant equal to 3.14, r is the radius, and h is the height of the cylinder.

Polymerization shrinkage (ΔV) in % was calculated according to the differences between the volume of the Teflon mold and the specimen, using the following equation:

$$\Delta V = \frac{\text{Vol}_{\text{mold}} - \text{Vol}_{\text{specimen}}}{\text{Vol}_{\text{mold}}} \times 100\%$$

where ΔV is the volume variation as a percentage (%), Vol_{mold} , is the volume of the Teflon mold, and $\text{Vol}_{\text{specimen}}$ is the volume of the specimen.

2.2. Optical coherence tomography

In this experiment, a commercially available OCT system was used (Spectral Radar SR-OCT: OCP930SR/Thorlabs, New Jersey, USA). The superluminescent diode (SLD) light source operates at a central wavelength of 930 nm. This system consists of

three main parts: a handheld scanning probe, a base unit, and a personal computer (PC) (Fig. 2). The base unit contains the SLD light source. A fiber optic coupler is used to direct the light from a broadband SLD source to the Michelson interferometer, which is located inside the handheld probe. Both probe and reference light travel back through the same fiber to the spectrometer and imaging sensor located in the base unit. The base unit is connected to the PC, which is equipped with two high-performance data acquisition cards. All required data acquisition and processing is performed via the integrated software package, which contains a complete set of functions for controlling data measurement, collection and processing, and for displaying and managing OCT image files. The maximum image depth is 1.6 mm and transverse scanning is 6.0 mm with an axial resolution of 6.2 μm .

A cylindrical Teflon mold (7 mm diameter \pm 0.5 mm height) was used to assess linear polymerization shrinkage. To execute the scans, insert and photoactivate the composites, the mold was fixed onto a sliding rail. A micrometric x , y , and z translator was attached to the scanning probe in order to dislocate it precisely. This was necessary to ensure OCT scanning of the entire mold. Because of the smaller size of the scan length (6.0 mm) compared with the diameter of the Teflon mold (7.0 mm), each scan was done at two distinct predetermined points.

At the beginning of each specimen preparation, the empty mold was scanned to ensure its accurate height. Resin composites were inserted into the mold it and then covered with a very thin microscope glass slab (0.13–0.16 mm thick). A thicker microscope glass slab (1.03 mm) was placed over the whole assembly and manually pressed against the mold to ensure

adequate resin accommodation inside the cavity and then it was removed. In a dark room, a second scan was performed to register the exact amount of uncured resin.

Photoactivation was performed using the established protocol, and the very thin microscope glass slab was then carefully removed from the upper side of the specimens. Fifteen minutes later, another scan was performed ($n=5$).

To measure the thickness of the composites, images were analyzed using the ImageJ program (Image Processing and Analysis in Java) [24]. Linear shrinkage was then calculated using the formula:

$$\text{linear shrinkage} = \frac{RC_{0\min} - RC_{15\min}}{RC_{0\min}} \times 100\%$$

where $RC_{0\min}$ is the mean resin thickness between points 1 and 2 when it is still unpolymerized, and $RC_{15\min}$ is the polymerized mean resin thickness between points 1 and 2.

The refractive index of all the test materials was also calculated using the previously obtained images. The refractive index was determined by applying the formula: refractive index = optical distance/real distance. The optical distance was obtained from the OCT images and the real distance refers to the real thickness of the samples, which was measured from the height of the Teflon molds confirmed by a digital caliper (0.01 mm). Two images (points 1 and 2) were generated for each sample and the refractive index was calculated for each point, which resulted in 10 measurements for each group. Mean values were calculated to obtain the refractive index of the material.

2.3. Archimedes principle

Volumetric shrinkage was determined by density measurements according to Archimedes Principle. Measurements were carried out using a digital analytical balance with a density determination kit (Marte AL 500, Minas Gerais, Brazil). To obtain stabilized readings the measurements were done in a temperature-controlled room ($T=25 \pm 1^\circ\text{C}$) and protected from air drafts and electrostatic influences [1].

The specimens were weighed in air and in water and the density in g/cm was calculated according to the equation:

$$\rho = \frac{m_{\text{water}}}{m_{\text{air}} - m_{\text{water}}} (\rho_{\text{water}} - \rho_{\text{air}}) + \rho_{\text{air}}$$

where ρ is the density of the material, m_{water} is the weight in grams (g) of the specimen in water, m_{air} is the weight in grams (g) of the specimen in air, ρ_{water} is the density of water at the exactly measured temperature in $^\circ\text{C}$ according to the density table for distilled water, and ρ_{air} is the density of air (0.0012 g/cm).

Five uncured sphere-shaped specimens each weighing 0.10 ± 0.02 g, were carefully hand made in such a way that trapped air bubbles were avoided. Since the uncured materials were rather sticky, a small mylar strip was used to handle the uncured material. The weight in air and water was previously determined. The weight of the whole assembly (resin + mylar strip) was then determined, first in air and then in water. Slight deformations of the material during the test were of no importance because they do not influence the density. Furthermore, the weighing process was very fast, so there was not much time for the material to flow. The mass of each material was

Table 2 – Mean values of polymerization shrinkage (%) and standard deviations (σ) of the materials studied. Different superscript letters indicate that the materials are statistically different at 5% using the Games–Howell test.

Resin	CMM	OCT	Archimedes
Filtek Z250 TM	4.83 (1.42) ^{BCD}	2.63 (0.66) ^C	-2.04 (-0.18) ^C
Filtek Z350 TM	4.45 (0.36) ^{CD}	1.02 (0.38) ^{AB}	-1.28 (-0.06) ^{AB}
Filtek P90 TM	1.13 (0.43) ^A	0.70 (0.01) ^A	-0.88 (-0.36) ^A
4 Seasons TM	3.01 (0.49) ^B	1.50 (0.07) ^{BC}	-1.35 (-0.33) ^{ABC}
Tetric Ceram TM	2.63 (1.07) ^{ABC}	1.94 (0.07) ^C	-0.94 (-0.27) ^A
Esthet-X TM	4.55 (1.28) ^{BCD}	1.65 (0.32) ^{BC}	-1.74 (-0.37) ^{BC}
TPH Spectrum TM	5.23 (0.94) ^D	-	-2.77 (-0.70) ^D

calculated by subtracting the mass of the mylar strip from the mass of the whole assembly. Then, the density of the uncured material (ρ_{unpol}) was computed.

To measure the density of the polymerized resin, five cylindrical specimens were made in a Teflon mold (7 mm \times 2 mm) and the upper side was covered with a mylar strip to avoid an oxygen inhibition layer [19]. Photoactivation was carried out using the established protocol. Specimens were weighed after 15 min of dry and dark storage. The percentage change in volume change (ΔV) after polymerization was calculated from the densities according to the equation:

$$\Delta V = \left(\frac{1}{\rho_{15\min}} - \frac{1}{\rho_{\text{unpol}}} \right) \frac{1}{\rho_{\text{unpol}}} 100\%$$

2.4. Statistical analysis

Statistical analysis was done using SPSS software 13.0 (Statistical Package for the Social Sciences, Chicago, USA). Means and standard deviations were calculated. Normal distributions were tested by the Kolmogorov–Smirnov test. One-way ANOVA was calculated to see if there were any differences between the groups. To evaluate the effect of the material and the method for measuring polymerization shrinkage, a two-way ANOVA was carried out and Levene's statistic was used to test for homogeneity of variances. Parametric test procedures were used for the final tests: the Tukey test in case of homogeneity of variances and the Games–Howell test where no variance homogeneity existed. Pearson's correlation analysis was also done between methods. Statistical significance for all tests was considered as $p < 0.05$.

3. Results

The results for polymerization shrinkage (%) are shown in Table 2. One way ANOVA rejected the null hypothesis for all three methods, showing that at least one of the groups differed from the rest ($p < 0.001$).

For CMM method, the post hoc Games–Howell test revealed significant differences between Filtek P90 and all the groups, except for Tetric Ceram ($p=0.211$) as shown by the different letters. Tetric Ceram on the other hand, only differed from TPH Spectrum ($p=0.036$) which presented the highest mean volumetric shrinkage values (5.23%).

Through OCT showed significant differences between Filtek P90 and all the groups except for Filtek Z350 ($p=0.513$).

Table 3 – Differences and mean comparisons between methods using the Games–Howell test (mean differences are shown in parentheses).

Methods	CMM	OCT	Archimedes
CMM	–	(2.116) $p < 0.001$	(2.118) $p < 0.001$
OCT	–	–	(0.002) $p = 1.000$
Archimedes	–	–	–

Again, Filtek Z350 only differed from Tetric Ceram ($p = 0.020$) and Filtek Z250 ($p = 0.029$) as shown by the different letters. Filtek Z250 had the highest mean linear shrinkage values (2.63%). Measurement of TPH Spectrum was not possible by this method, because we were not able to observe the bottom of the mold and, consequently, could not measure the original height of the uncured resin composite.

For Archimedes Principle, TPH spectrum had the highest mean volumetric shrinkage values (2.77%) and also differed from all the other groups when the post hoc Games–Howell test was done, as shown by the different letters. Filtek P90 had the lowest mean volumetric shrinkage. Negative values indicate that the material underwent volume reduction.

Two-way ANOVA revealed a significant influence of the tested material and the method used ($p < 0.001$). The two independent variables also showed significant interactions with respect to the target variable (shrinkage).

Table 3 shows the differences and mean comparisons between methods using the Games–Howell multiple comparisons test. Shrinkage values obtained with CMM differ from the other methods ($p < 0.001$); the results for OCT and Archimedes were statistically similar ($p = 1.000$).

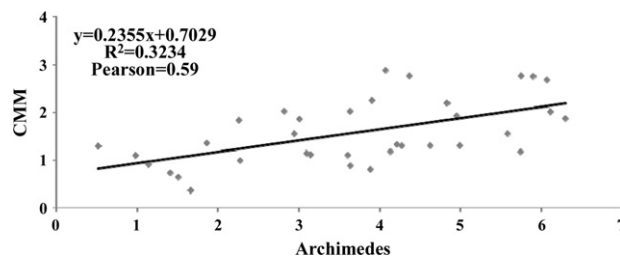
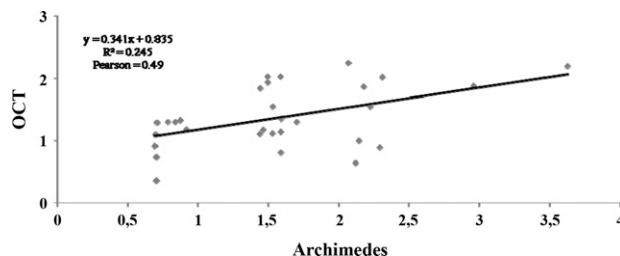
Linear regression curve fit between methods was done [25]. Direct linear relationships were verified although the regression coefficients were fairly low (Archimedes/CMM method $R^2 = 0.323$; Archimedes/OCT $R^2 = 0.245$). Fig. 3 shows the correlation test between Archimedes and CMM. From this graph, it can be seen that when a given composite presented higher shrinkage values when the CMM method was applied, there was also an increase in the results obtained when the Archimedes method was applied, but in a lower proportion (0.57). Moreover, the correlation test between Archimedes and OCT presents an even smaller relationship (0.49, Fig. 4).

Table 4 gives the refractive index of all test materials at 0 and 15 min.

Table 4 – Mean values of the refractive index of the materials at 0 (unpolymerized composite) and at 15 min (polymerized composite).

Material	Refractive index	
	RC _{0 min} (unpolymerized)	RC _{15 min} (polymerized)
Filtek Z250	1.5610	1.5187
Filtek Z350	1.3793	1.3690
Filtek P90	1.6620	1.6429
Esthet-X	1.5672	1.5354
TPH-Spectrum	0.000 ^a	1.5408
4 Seasons	1.5142	1.4823
Tetric Ceram	1.5533	1.5216

^a Optical distance measurements were not realized.

**Fig. 3 – Linear regression curve fit between Archimedes and the CMM method.****Fig. 4 – Linear regression curve fit between Archimedes and the OCT method.**

4. Discussion

Reducing polymerization shrinkage is a primary goal toward diminishing stress generation at the bonded interface. Nevertheless, assessing the real shrinkage that takes place with a particular resin composite remains a challenge. Many methods can be used for such measurements, and for each one, a distinct aspect of polymerization shrinkage is measured. Therefore, to generate reliable shrinkage values it is important to apply different types of measurement principles and not rely on a single protocol [25].

From our results, we strongly agree with previous studies that the value of the amount of shrinkage of a resin composite depends on the method used to measure that shrinkage [26]. However, each of the several different methods for measuring the shrinkage that occurs during polymerization, or curing, relies on a different physical basis for the measurement [8].

Inherently, methods measuring multi-axial dimensional change measure volumetric shrinkage. However, volumetric deformation can be mathematically derived from linear

values. Shrinkage measurements can also record the total shrinkage (i.e. pre- and post-gel shrinkage) or only post-gel contraction. The latter requires a sensor that ignores viscous flow and is sensitive only to shrinkage of a solid with measurable stiffness [8].

By using Archimedes method, the entire volumetric change is captured, directly providing three-dimensional volumetric shrinkage [25]. The GMM method is only able to measure post-gel contraction through dimensional changes in the height and width of the samples, which are then converted to a three-dimensional value. Using OCT, it was only possible to measure linear shrinkage, considering the changes in the thickness of the materials.

In addition, using OCT, simultaneous time-resolved measurements of the group refractive index, optical thickness and physical thickness of a dental composite sample before, during and after the curing process can be made. This facilitates the optimization of the optical and physical characteristics of the sample. Since light passes through the sample, the refractive index is an average over index contributions from the filler and the resin. Earlier works suggest that the change in measured refractive index relates to the monomer-polymer conversion, because the contribution from the filler particles remains constant [27].

In this study, a reduction in the refractive index of the composites was observed as polymers were formed. It can be shown that the change in refractive index is directly proportional to the change in physical thickness. The results from a previous study showed exactly the opposite [27]. It was also stated that if shrinkage is entirely due to polymerization, the linearity of the thickness-index relationship therefore has the potential to provide a measure of the degree of polymerization. However, the complexity of the optical transmission properties of the curing specimen warrants further investigation, with explicit consideration of the degree of polymerization.

Factors that could help to explain the differences between the methods have been previously discussed in the literature, e.g., measurement of a different aspect of the shrinkage process (total vs. post gel, volumetric vs. linear). Variation in boundary conditions could also explain these dissimilarities. Only the total shrinkage was measured for the three methods tested here. Linear measurements were taken using OCT. Volumetric shrinkage was acquired using Archimedes principle. Yet, very small differences were found in the boundary conditions, or constraint, applied to the composite specimen by each method. This is important because the degree of constraint applied to the external boundaries of a deforming body affects the potential for deformation. It is expected that the constraint imposed by each shrinkage measurement method affects the net shrinkage measured [8]. The degree of constraint did not play a fundamental role on the shrinkage values given that we standardized the dimensions of the specimens and mold material and size. The only differences were found for OCT measurements, which were done in a thinner mold (0.5 mm) because of the intrinsic difficulty of visible light passing through the resin composites at 2 mm.

Specimen size is a limitation for both experimental methods. Coordinate measuring machines are mainly built for much larger samples than the ones used here. The limitation in evaluating smaller samples is related to the size of ruby

probes. Even when using very small probes, there is a need for a bigger contact area than the probe size itself in order to guarantee proper probe/sample contact. When evaluating small samples, special attention must be given to specimen fixation on the granite table. Because the probe moves according to a joystick command to contact the sample, there is a necessity for proper specimen fixation. This fixation should be on the lateral side, ensuring that the specimens are in direct contact with the granite table and/or a flat glass plate. Free lateral areas must also be present so that the probe can make contact with the specimen.

The opposite occurs when making measurements with OCT. Depending on the optical properties of the sample, specimen thickness can be a major drawback. Previous pilot studies confirmed that at 0.5 mm, visible light can pass through the entire thickness of the sample and backscatter. Depending on the optical setup, the linear shrinkage results must be calculated in a second moment using computerized imaging processing and analysis (ImageJ). However, the OCT method is still advantageous considering the technique's potential for performing *in vivo* measurements [28].

Specimen size and geometry are not such a problem when applying Archimedes principle. However, this method is subject to other variables that directly influence the results such as the presence of voids inside the specimen or air bubbles on its surface [12]. Although it is a relatively inexpensive method for determining the shrinkage of dental composites, it is multi-step and time consuming. Other authors state that it should only be used at least 2 min after starting the light-curing process [29]. This is the only method for measuring polymerization shrinkage that has published standards for execution [30].

To better understand the real shrinkage values, we have gathered data published within the last 10 years (Table 5). Comparing our results with those from the pooled data, it can be seen that the OCT values were comparable with other previously published data and with the data obtained here when applying Archimedes principle. Different resolutions were found between these new tested methods. Although GMM has a 2.0- μm measurement uncertainty, the OCT setup used here has a 6.2- μm axial resolution. Other methods, such as the use of a linear variable displacement transducer (LVDT), present even higher resolution (0.01 μm). However, these resolutions or accuracy do not seem to have influenced our results (Table 5).

Because of the inherent differences between methods, comparison of the shrinkage values was very difficult. We therefore hoped to acquire additional information on the basis of a clear ranking of the polymerization shrinkage measurements of the materials [35]. However, only the ranking for materials with the lowest (Filtek P90) and higher shrinkage (Filtek Z250 and TPH Spectrum) was coincident between methods.

Because of the clinical significance of polymerization shrinkage, efforts have been made to modify the vectors of the resultant stresses in favor of the restoration. These efforts are related either to the restoration technique per se or to the development of new materials. For the first task, different curing protocols have been proposed such as soft-start, pulse, step and exponential curing or changing the curing direction. Incremental layering and use of low-filled liners as a means

Table 5 – Summary of previously reported values for polymerization shrinkage of the evaluated composites.

Material	Method	Irradiance (mW/cm ²), time	Shrinkage (%), SD	Observations	Reference
Filtek Z250	AcuVol	1600, 40 s	2.75 ^a		31
	AcuVol	1600, 20 s	3.30 ^a		32
	Archimedes	?	2.20 ^a		25
	Bonded Disc	?	1.80 ^a		25
	Bonded Disc	800, 40 s	2.44	At 37 °C	33
	Mercury Dilatometry	750, 40 s	2.22 (0.03)	Values at 15 min	3
Filtek Z350	AcuVol	1600, 40 s	2.50 ^a	Filtek Supreme ^b	31
	Archimedes	?, 180 s Light curing chamber	1.68 (0.25)	Filtek Supreme ^b	34
	Mercury Dilatometry	750, 40 s	2.38 (0.03)	Values at 15 min Filtek Supreme ^b	3
Filtek P90	AcuVol	1600, 40 s	1.50 ^a	Filtek LS ^c	31
	Archimedes	?	0.94		25
	Bonded Disk	?	0.99		25
Esthet-X	AcuVol	1600, 40 s	3.00 ^a		31
	AcuVol	1600, 20 s	3.30 ^a		32
	Archimedes	?, 180 s Light curing chamber	2.60 (0.22)	Values at 1 h	34
TPH-Spectrum	Archimedes	?	3.30 ^a		25
	Archimedes	703, 40 s	2.128 (0.12)	Using trilight standard	29
	Bonded Disk	?	2.50 ^a		25
	Bonded Disk	703, 40 s	1.995 (0.03)	Using trilight standard	29
	Mercury Dilatometry	750, 40 s	3.04 (0.09)	Values at 15 min	3
Tetric Ceram	Archimedes	?	3.00 ^a		25
	Archimedes	?, 3 min light oven	3.09 (0.13)		35
	Archimedes	?, 180 s light curing chamber	2.56 (0.23)	Values at 1 h	34
	Bonded Disk	?	2.27		25
	Bonded Disk	400, 40 s	2.11 (0.15)		36
	Linometer	?, 40 s	1.94 (0.04)		35
	Mercury Dilatometry	750, 40 s	3.02 (0.12)	Values at 15 min	3
	Mercury Dilatometry	?, 40 s	2.40 (0.03)		35

No values were found for 4 Seasons.

^a Approximate values obtained by analyzing graphs.

^b Composition of Filtek Z350 and Filtek Supreme is the same.

^c Composition of Filtek LS and Filtek P90 is the same.

of stress reduction have also been advocated. For the second task, a lot of interest has focused on the development of low-shrinking materials by introducing new filler technology and monomer chemistry [37].

Low shrinkage values were obtained for Silorane Filtek P90. This material is one of a totally new class of compounds for use in dentistry. Siloranes are obtained from the reaction of oxirane and siloxane molecules. The novel resin is considered to have the two key advantages over the individual components: low polymerization shrinkage due to the ring-opening oxirane monomer and increased hydrophobicity due to the presence of siloxane species [38]. As a result, the new silorane-based material has the ability to compensate for shrinkage by opening the oxirane ring during polymerization [39].

The initiation system was also modified. Instead of using a two-component system as in methacrylate-based resin, it uses a three-component initiating system comprising camphorquinone, an iodonium salt, and an electron donor [39]. In the redox process, the electron donor decomposes the iodonium salt to an acidic cation, which then starts the ring-opening polymerization process. As in the methacrylate-based composite, the silorane-based composite also contains camphorquinone so that current dental curing units can be used for polymerization [7].

The high hydrophobic nature also limits water sorption favoring long-term intraoral physical strength of the com-

posite. In addition, hydrophobic materials tend to absorb much less dye from the daily nutrition and are much less sensitive to exogenic staining than hydrophilic materials [25].

All methacrylate-based resins shrink to some extent, and contraction can be reduced by using monomers with a very large molecular weight. Viscosity is an indicator of the ability of molecules to flow and a high viscosity value indicates the presence of molecular interactions that may account for the decreased flexibility of the corresponding polymeric network [40]. BisGMA is the most commonly used organic matrix with very high viscosity as a result of the hydrogen bonding interactions that occur between the hydroxyl groups and the monomer molecules. Therefore, BisGMA must be diluted with more fluid monomers to provide the proper viscosity for use in dental composites as occurs with 4 Seasons and Tetric Ceram [41].

The incremental addition of a lower molecular weight and lower viscosity monomer such as EGDMA and TEGDMA leads to higher conversion and volumetric shrinkage. This occurs because of a reduction in the mixture's initial viscosity, improving reaction medium mobility, which favors conversion. However, the increase in volumetric shrinkage comes not only from the increased conversion, but also from the increased initial molar concentration of reactive groups given by TEGDMA's lower molecular weight [42].

The BisEMA monomer is a viscous monomer structurally similar to BisGMA, but without the two pendant hydroxyl groups that participate in hydrogen bonding and are responsible for the extremely high viscosity of BisGMA. Filtek Z250, Filtek Z350 and Esthet-X are examples of composites with BisEMA in their composition. The UDMA monomer is more viscous than TEGDMA and BisEMA, because of the hydrogen bonding between the $-NH-$ and $-C=O$ groups. However, it is less viscous than BisGMA, since imino groups form weaker hydrogen bonds compared with hydroxyl groups [40]. Moreover, UDMA is more reactive than BisGMA, as a result of increased molecular flexibility and chain transfer reactions through the $-NH$ group. This allows for higher rates of polymerization and for a higher conversion to be achieved before the onset of gelation, as well as a higher degree of crosslinking [42]. Apart from siloranes, all evaluated materials have urethane-modified monomers in their composition.

However, it is interesting to observe that the low shrinkage values for siloranes in all evaluations gave similar statistical results to methacrylate-based composites such as Tetric Ceram, Filtek Z350 and/or 4 Seasons.

High polymerization shrinkage values were achieved by TPH Spectrum. This microhybrid methacrylate-based composite is composed only of urethane-modified BisGMA; this monomer corresponds to a BisGMA molecule with urethane bonds that tend to lower the viscosity of BisGMA, raising the mobility of its molecules during the polymerization of the organic matrix and, possibly, increasing the degree of conversion and leading to higher polymerization shrinkage [43].

The influence of the inorganic component on polymerization shrinkage has also been reported. Concentration, shape, and size are factors that have reportedly influenced or may influence the amount of contraction that a polymerizing composite undergoes. Polymerization shrinkage may be greater for composites with irregular shape due to the low interaction between the particles [44]. Similarly, large fillers tend to increase volumetric shrinkage because of the smaller area-to-volume ratio of the particles and the great interparticle spacing left for the resin matrix. Filler loading can be deceiving, however, because it may indicate the presence of pre-polymerized filler particles. Resin composites typically benefit from the use of pre-polymerized filler particles by having lower polymerization shrinkage [32]. The use of non-silanated fillers has also been suggested as a stress-relieving mechanism inside composites [37].

The shrinkage behavior of nanoparticle/nanohybrid composites can also be seen from our results. The data showed no or small differences between them and conventional microhybrid resins. Nonetheless, comparison of the properties of commercial materials is challenging because all the constituents are rarely disclosed [45]. Filler morphology, resin formulations and photoinitiation chemistry differ greatly between brands.

5. Conclusions

Methods for measuring polymerization shrinkage are quite unique, each having its own advantages and disadvantages. Considering the great variations between the results obtained,

reported values can only be used to compare materials within the same method. Notwithstanding, it is possible rank composites for polymerization shrinkage and to relate these data from different test methods. Independently of the method used, reduced polymerization shrinkage was found for silorane resin-based composite.

REFERENCES

- [1] Koplín C, Jaeger R, Hahn P. Kinetic model for the coupled volumetric and thermal behavior of dental composites. *Dental Materials* 2008;24(8):1017–24.
- [2] Petrovic LM, Atanackovic TM. A model for shrinkage strain in photo polymerization of dental composites. *Dental Materials* 2008;24(4):556–60.
- [3] Kleverlaan CJ, Feilzer AJ. Polymerization shrinkage and contraction stress of dental resin composites. *Dental Materials* 2005;21(12):1150–7.
- [4] Peutzfeldt A, Asmussen E. Determinants of in vitro gap formation of resin composites. *Journal of Dentistry* 2004;32(2):109–15.
- [5] Cadenaro M, Biasotto M, Scuor N, Breschi L, Davidson C, Di Lenarda R. Assessment of polymerization contraction stress of three composite resins. *Dental Materials* 2008;24(5):681–5.
- [6] Watts DC, Satterthwaite JD. Axial shrinkage-stress depends upon both C-factor and composite mass. *Dental Materials* 2008;24(1):1–8.
- [7] Ilie N, Hickel R. Silorane-based dental composite: behavior and abilities. *Dental Materials Journal* 2006;25(3):445–54.
- [8] Sakaguchi RL, Wiltbank BD, Shah NC. Critical configuration analysis of four methods for measuring polymerization shrinkage strain of composites. *Dental Materials* 2004;20(4):388–96.
- [9] Watts DC, Cash AJ. Determination of polymerization shrinkage kinetics in visible-light-cured materials: methods development. *Dental Materials* 1991;7(4):281–7.
- [10] De Gee AF, Davidson CL, Smith A. A modified dilatometer for continuous recording of volumetric polymerization shrinkage of composite restorative materials. *Journal of Dentistry* 1981;9(1):36–42.
- [11] Sharp LJ, Choi IB, Lee TE, Sy A. Volumetric shrinkage of composites using video-imaging. *Journal of Dentistry* 2003;31(2):97–103.
- [12] Tiba A, Charlton DG, Vandewalle KS, Ragain Jr JC. Comparison of two video-imaging instruments for measuring volumetric shrinkage of dental resin composites. *Journal of Dentistry* 2005;33(9):757–63.
- [13] Amore R, Pagani C, Youssef MN, Anauate Netto C, Lewgoy HR. Polymerization shrinkage evaluation of three packable composite resins using a gas pycnometer. *Pesquisa Odontologica Brasileira* 2003;17:273–7.
- [14] Pereira RA, Araújo PA, Castañeda-Espinosa JC, Mondelli RFL. Comparative analysis of the shrinkage stress of composite resins. *Journal of Applied Oral Sciences* 2008;16(1):30–4.
- [15] Orrego RMM, Di Giacomo B, Abackerli AJ. An overview on the kinematic modeling of coordinate measuring machines (CMMs). *Revista de Ciência & Tecnologia* 2001;8(18):31–43.
- [16] Seymour K, Zou L, Samarawickrama DYD, Lynch E. Assessment of shoulder dimensions and angles of porcelain bonded to metal crown preparations. *Journal of Prosthetic Dentistry* 1996;75(4):406–11.
- [17] Baek JH, Na J, Lee BH, Choi ES, Son WS. Optical approach to the periodontal ligament under orthodontic tooth movement: a preliminary study with optical coherence tomography. *American Journal of Orthodontics and Dentofacial Orthopedics* 2009;135(2):252–9.

- [18] Otis LL, Al-Sadhan RI, Melers J, Redford-Badwal D. Identification of occlusal sealants using optical coherence tomography. *Journal of Clinical Dentistry* 2003;14(1):7–10.
- [19] Chutinan S, Platt JA, Cochran MA, Moore BK. Volumetric dimensional change of six direct core materials. *Dental Materials* 2004;20(4):345–51.
- [20] Rüttermann S, Krüger S, Raab WH-M, Janda R. Polymerization shrinkage and hygroscopic expansion of contemporary posterior resin-based filling materials—a comparative study. *Journal of Dentistry* 2007;35(10):806–13.
- [21] Moznar N, Fischer UK, Angermann J, Rheinberger V. A partially aromatic urethane dimethacrylate as a new substitute for Bis-GMA in restorative composites. *Dental Materials* 2008;24(5):694–9.
- [22] Rueggeberg FA. Contemporary issues in photocuring. *Compendium of Continuing Education in Dentistry* 1999;25:S4–15 [quiz S73].
- [23] Calheiros FC, Sadek FT, Braga RR, Cardoso PEC. Polymerization contraction stress of low-shrinkage composites and its correlation with microleakage in class V restorations. *Journal of Dentistry* 2004;32(5):407–12.
- [24] Rasband WS. ImageJ; 2006. Retrieved online July 15, from: <http://rsb.info.nih.gov/ij/>.
- [25] Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. *Dental Materials* 2004;21(1):68–74.
- [26] Davidson CL, Feilzer AJ. Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. *Journal of Dentistry* 1997;25(6):435–40.
- [27] Tomlins PH, Palin WM, Shortall AC, Wang RK. Time-resolved simultaneous measurement of group index and physical thickness during photopolymerization of resin-based dental composite. *Journal of Biomedical Optics* 2007;12(1):014020.
- [28] Melo LSA, Araujo RE, Freitas AZ, Zezell D, Vieira Jr ND, Girkin J, Hall A, Carvalho MT, Gomes ASL. Evaluation of enamel dental restoration interface by optical coherence tomography. *Journal of Biomedical Optics* 2005;10:064027.
- [29] Uhl A, Mills RW, Rzanny AE, Jandt KD. Time dependence of composite shrinkage using halogen and LED light curing. *Dental Materials* 2005;21(3):278–86.
- [30] German Standard DIN 13907:2007, Zahnheilkunde – Polymerisationsschrumpfung von Füllungswerkstoffen.
- [31] Lien W, Vandewalle KS. Physical properties of a new silorane-based restorative system. *Dental Materials* 2009;26(4):337–44.
- [32] Blackham JT, Vandewalle KS, Lien W. Properties of hybrid resin composite systems containing prepolymerized filler particles. *Operative Dentistry* 2009;34(6):697–702.
- [35] Rosin M, Urban AD, Gärtner C, Bernhardt O, Splieth C, Meyer G. Polymerization shrinkage-strain and microleakage in dentin-bordered cavities of chemically and light-cured restorative materials. *Dental Materials* 2002;18(7):521–8.
- [37] Papadogiannis D, Kakaboura A, Palaguias G, Eliades G. Setting characteristics and cavity adaptation of low-shrinking resin composites. *Dental Materials* 2009;25(12):1509–16.
- [38] Ilie N, Hickel R. Macro-, micro- and nano-mechanical investigations on silorane and methacrylate-based composites. *Dental Materials* 2009;25(6):810–9.
- [39] 3M ESPE, Filtek LS technical profile, 2009; <http://multimedia.com/mws/mediaserver>.
- [40] Marchesi G, Breschi L, Antonioli F, Di Lenarda R, Ferracane J, Cadenaro M. Contraction stress of low-shrinkage composite materials assessed with different testing systems. *Dental Materials* 2010, doi:10.1016/j.dental.2010.05.007.
- [41] Chen M-H. Update on dental nanocomposites. *Critical Reviews in Oral Biology & Medicine* 2010;89(6):549–60.
- [42] Gonçalves F, Pfeifer CCS, Stansbury JW, Newman SM, Braga RR. Influence of matrix composition on polymerization stress development of experimental composites. *Dental Materials* 2010;26(7):697–703.
- [43] Obici AC, Sinhoreti MAC, Goes MF, Consani S, Sobrinho LC. Effect of photo-activation method upon polymerization shrinkage of restorative composites. *Operative Dentistry* 2002;27(1):192–8.
- [44] Adabo GL, Cruz CAS, Fonseca RG, Vaz LG. The volumetric fraction of inorganic particles and the flexural strength of composites for posterior teeth. *Journal of Dentistry* 2000;31(5):353–9.
- [45] Leprince J, Palin WM, Mullier T, Devaux J, Vreven J, Leloup G. Investigating filler morphology and mechanical properties of new low-shrinkage resin composite. *Journal of Oral Rehabilitation* 2010;37(5):363–76.