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Volumetric change of flowable composite resins due to polymerization as measured with an electronic mercury dilatometer

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Abstract

Background: To determine the total volumetric change and the relative speed of shrinkage of bulk fill flowable composites during polymerization.

Materials and methods: A specially designed electronic mercury dilatometer was used to determine the volumetric change. The light intensity was 500mW/cm^2. The mercury dilatometer measured the volumetric change every 0.5 seconds during the 35 second irradiation exposure time. The materials tested were Z250 as standard and control. Four bulk fill flowable composites were tested.

Results: The sequence of total volumetric change was found to be: Z250 < Filtek bulk fill < Xtra-Base bulk fill < SDR < Venus bulk fill. The speed of shrinkage of the bulk fill flowables was faster than that of Z250, while the 2 flowables with the highest shrinkage speed (SDR and Venus) also had the highest total volumetric change. Of the different materials tested the volumetric change of Z250 (1.13%) was the lowest and significantly less ($p<0.05$) than that of SDR (1.55%) and Venus (1.72%). The material with the highest filler content (Z250) also showed the lowest shrinkage (1.13%) but this effect could not be seen in the flowables. In general, it was found that a 35 second irradiation period (with a light intensity of 500mW/cm^2) was satisfactory for complete polymerization of the resins.

Conclusions: The volumetric changes and speed of shrinkage were higher for all 4 bulk fill flowable composites than for Z250. SDR and Venus flowables had the fastest and highest volumetric shrinkage.

Clinical significance: The manufacturers of bulk fill flowable composites advocate filling layers of 4mm. However, because of the high shrinkage values found in this study it should be suggested that the standard 2mm layer increments still be used.

Keywords: Volumetric change, flowable composites, mercury dilatometer, polymerization, bulk fill

Introduction

During polymerization the distance between groups of atoms/ molecules decreases with a resultant volume change that is known as shrinkage [1-3]. Polymerization shrinkage as low as 2% in composites may generate enough tension to destroy the marginal integrity between the restoration and the tooth structure which could result in micro-leakage, post-operative sensitivity and/or the failure of the restoration [4-6].

However, to minimize volumetric shrinkage, dental material manufacturers previously advised placing composite resins in increments not larger than 2-3mm before it is polymerized. Nowadays, manufacturers are becoming bolder with suggested increments of up to 4mm in regard to the bulk fill flowable composites [7-11]. This method of placement of bulk fill flowable composites, could pose a problem if the shrinkage of the material is too large and allows the disruption of the integrity of the tooth-restoration interface.

Various techniques are available to measure the volumetric change which occurs during irradiation with a curing light [12-15]. An electronic mercury dilatometer proved to be accurate in measuring polymerization shrinkage [1,12-18,35,39]. The volumetric shrinkage measured by the electronic mercury

dilatometer is linear and the volumetric change is measured as the total percentage shrinkage that occurred between the pre- and post-gel phases. Examples of various volumetric measuring techniques are the mercury dilatometer, water dilatometer, linear techniques and the pycnometer. A disadvantage with the utilization of dilatometers is that they are extremely sensitive to variations in temperature [14,19]. Oberholzer et al., [15] described a specially designed electronically controlled mercury dilatometer which measured change in volume of the sample every 0.5 seconds.

Studies were completed on varying irradiation techniques to decrease polymerization shrinkage and polymerization stress. Some of these techniques resulted in a low initial conversion rate of the organic matrix. However, the moment the resin material became rigid, the internal stresses and polymerization stress started to increase [8,20]. It has been established that exposures not higher than 500 mW/cm^2, were able to provide a sufficient combination of irradiance and exposure time [15,21]. It was found that conversion rate resulting in carbon double bond formation can range from 55-75% under conventional irradiation conditions of 500mW/cm^2 [22,23].

In an attempt to decrease volumetric shrinkage, an increase
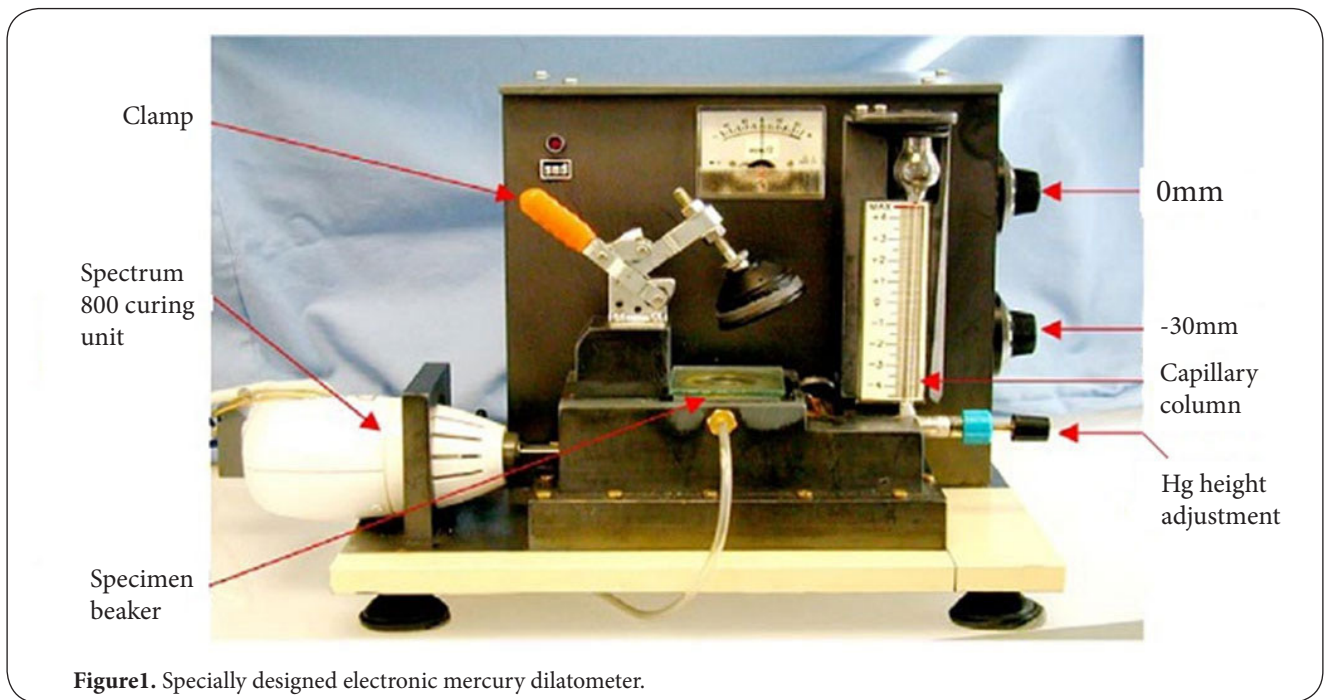
Figure1. Specially designed electronic mercury dilatometer.

in the molecular weight of the organic matrix was suggested [24-27]. Furthermore, by increasing the filler content the resulting contraction stress that developed was found to be directly proportional to the filler content regardless of the matrix [20,28]. Therefore, the purpose of this study was to determine the relative volumetric change and the speed of shrinkage of bulk fill flowable composites relative to the composite Z250.
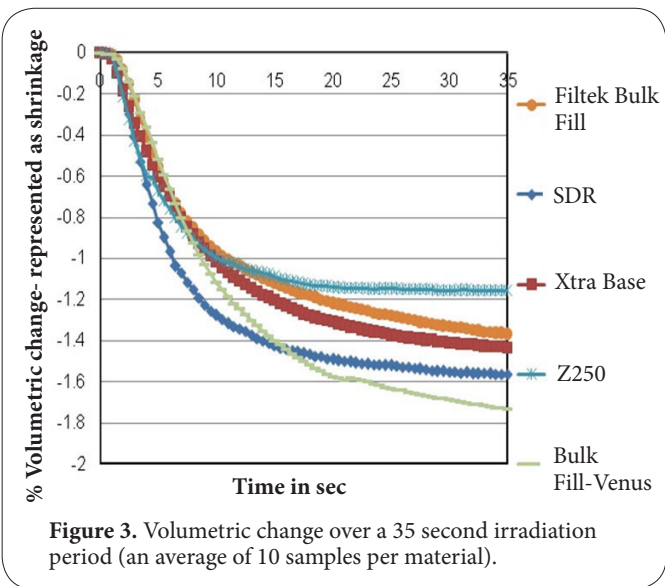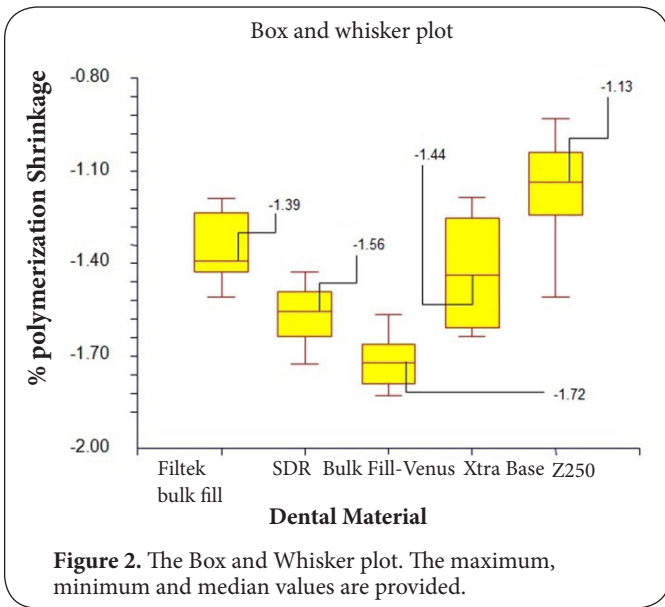
Materials and methods

The composite Z250 by 3M ESPE (Massachusetts, USA) was used as the standard control material. Furthermore, the shrinkage over time of four newly developed bulk fill flowable composites was measured.

The bulk fill flowable composites consisted of Smart Dentin Replacement (SDR) by Dentsply/Caulk (Milford, Germany), Venus bulk fill by Haraeus Kulzer (Hanau, Germany), Filtek bulk fill flow by 3M ESPE (Massachusetts, USA) and Xtra base bulk fill flowable by Voco (Cuxhaven, Germany). Volumetric change was measured with a specially designed electronic mercury dilatometer (**Figure 1**) [15] .The volumetric change due to polymerization in the dental resin material is measured as a voltage change by a pressure sensitive transducer. An analog to digital converter creates data that is transmitted from the pressure sensor to RS232 format - where the computer creates a graph of volumetric change in Microsoft Excel, From the data collected every 0.5 seconds over the 35 seconds from the curing light irradiation period the graph has time in seconds on the X-axis and the percentage of volumetric change on the Y-axis. All samples were cured for 35.0 seconds at 500mW/cm^2 with a Dentsply/Caulk Spectrum 800 halogen curing light in order to standardize the curing

process. The output was monitored with a Caulk (Milford, Germany) radiometer to ensure 500mW/cm^2± 50mW/cm^2. Calibration of the modified mercury dilatometer was done prior to every specimen test. Ten sample specimens of each material were tested. The Teflon specimen holder has a hole with a diameter of 5.0mm and a height of 2.5mm resulting in the specimen volume in the Teflon holder of 49.087mm^3. Briefly, the specimen was placed in the dilatometer and the clamp closed. The calibration was achieved by adjusting the mercury column. The curing light was activated by the computer when the mercury dilatometer had a stable environment for 5.0 seconds. The polymerization shrinkage of the resin material and the resultant volumetric change was measured every 0.5 seconds. The dilatometer was kept in a temperature controlled incubator at the 25°C ± 1°C [29]. The baseline effect of the curing unit was established prior to each set of experimental set-ups and the data corrected accordingly [21]. This correction resulted in the volumetric shrinkage that is presented for each material to be the true volumetric change due to polymerization only. Therefore only the effect of polymerization shrinkage from a monomer to a polymer remained [21,29,30].

Results

The total volumetric change for all ten samples of each material was presented as a combination in the Box and Whisker plot (**Figure 2**). Each Box and Whisker plot gives the maximum and minimum values. The intermediary box gives the range of 50% of the values and the solid line in each box indicates the median value for the 10 samples. The sequence of total volumetric change according to the shrinkage values

Figure 2. The Box and Whisker plot. The maximum, minimum and median values are provided.

Figure 3. Volumetric change over a 35 second irradiation period (an average of 10 samples per material).

after 35 seconds was: Z250< Filtek < Xtra base< SDR< Venus. The Kruskal-Wallis multiple-comparison test was used to show statistical significant differences in the total volumetric change amongst materials. The results (**Figure 2**) indicated that SDR and Venus bulk fill had significantly more volumetric shrinkage compared to Z250. Z250 shrank 1.13% and Venus bulk fill had the largest volumetric shrinkage of 1.72%.

The Tukey-Kramer multiple comparison test on the rate of shrinkage slopes (**Figure 3**) showed that at a 1.5-5.0 second time period, the slope of SDR was significantly (p<0.05) steeper (shrank the fastest) than that of all the other materials. At the time slot (5.5-20.0 seconds) Venus shrank the fastest (steepest slope). For the 20.5-25.0 period Z250 shrank significantly slower than Filtek, Venus and Xtra base but not significantly

slower than SDR. When the polymerization rate (slope) of Z250 was considered for the time period 20.5-30.0 seconds, it was found that the rate of polymerization shrinkage of all the bulk fill flowable composites tested were statistically significantly faster than that of Z250.

Discussion

Oberholzer et al., developed the dilatometer used in this study [**15**]. The main advantage of the dilatometer was that the change of the mercury height in the capillary could be measured electronically, instead of manual viewing. Furthermore, the electronic dilatometer enables measurements to be made on samples regardless of their shape and size. It was concluded [**15**] that the exothermic reaction from the small sample used was negligible and did not affect the volumetric change. The additional volumetric change that occurs due to the light source could also be determined and the real volumetric change calculated.

From the literature many factors might have an influence on the volumetric shrinkage of a material i.e., filler content, filler size, type of monomers, monomer content, organic matrix and type, and organic matrix conversion factors. The highest percentage volumetric shrinkage (**Figure 3**) for all 5 materials occurred approximately within the first 10.0 seconds. Furthermore, it can be seen that most (~ 90%) of the polymerization shrinkage for all 5 different materials took place in the first 20 seconds and the degree of polymerization was generally completed after 35 seconds of constant irradiation. Davidson [**12**] also reported that 90% of the shrinkage of composites took place during the first 20 seconds. However, when the sequence of shrinkage (Filtek < Xtra base < SDR < Venus) of the 4 bulk flowables was compared to their filler content (**Table 1**) no clear trend could be seen. Furthermore, the sizes of the fillers alone (**Table 1**) did not seem to show a clear effect on the shrinkage values, although Z250 with an average filler size of 0.6 µm showed a lower shrinkage (1.16%) relative to SDR with a higher average filler size of 4.2 µm. Unfortunately, the average filler sizes of the other flowables were not stipulated by the manufacturers and their possible effects on shrinkage could not be discussed. In general, the rate of polymerization shrinkage (**Figure 3**) for all the bulk fill flowable composites was faster than the control composite Z250.

The literature also showed that in general the higher the monomer content and the more flowable, the higher the shrinkage [**12,25,31-35**] and the faster the conversion rate to the gel phase [**18,20,22**]. Again, without the necessary information (**Table 1**) this could not be meaningfully discussed. The shrinkage curve (**Figure 3**) for Venus over the whole 35 second period was the most fluent which indicated a steady shrinkage which might have a positive effect on bond strength.

The slopes of the shrinkage rates over the first 5 seconds did not differ significantly. However, over the 5-15 second period, Venus and SDR shrank the fastest after which period

Table 1. Information on the various resin composites and % volumetric shrinkage found.

Dental material	Inorganic filler	Organic resin matrix	Filler size μm	% filler wt.	Shrinkage
Z250 (3M ESPE) Lot 176833 exp 2013-05	Zirconia/ silica	bisGMA (1-10%), UDMA (1-10%), BisEMA (1-10%), TEGDMA (<5%)	0.01-3.5 (Average size 0.6)	78	1.13%
SDR bulk flow (Dentsply/ Caulk) Lot 110429. exp. 2013-04	Barium-alumino-fluoro-borosilicate glass; Strontium alumino-fluoro-silicate glass	SDR patented urethane (<25%), TEGDMA (<10%), EPBADMA (<10%)	Average size 4.2	68	1.55%
Venus Bulk Fill (Haraeus Kul-zer) Lot 010031 exp. 2014-08	barium- alumina-fluoro-silicate, YbF3, Silica.	UDMA (Not available), EPBADMA (Not available)	0.02-5	65	1.72%
Filtek bulk flow (3M ESPE) lot N356852 exp. 2015-02	YBF3 filler Zirconia / silica	UDMA (10-20%), bisGMA (1-10%), bisEMA (6) (1-10%), procrylat resins (10-20%), TEGDMA (<1%)	0.1-5 0.01-3.5	64.5	1.39%
Xtra Base bulk flow (Voco) Lot 1201096	Not available from manu-facturer	bisGMA (10-25%), UDMA (10-25%)	Not available	75	1.44%

Table 2. Molecular weight of individual monomers.

Resin present in material	Molecular weight g/mol
UDMA (urethane dimethacrylate)	470.55
SDR-UDMA	849
TEGDMA3 (6-dioxaoctamethylene-dimethacrylate)	286.32
bisGMA (bis-phenol glycidylmethacrylate)	512.59
Bisema6 (bisphenol A polyethylene glycol diether dimethacrylate).	496.58
EBADMA (2-propenoic acid 2-methyl-1,1'-[(1-methylethylidene) bis(4,1-phenylene-oxy-2,1-ethanediyl)] ester	496.58
EPBADMA	452.53
Procrylate2,2-bis[4-(3-methacryloxypropoxy) phenyl]propane	480.59

they all levelled out to about the same slope and shrinkage rate. After about 15 seconds the shrinkage rate of SDR decreased at which stage Venus began to shrink at a faster rate than SDR. The speed of shrinkage (slopes) of the other 2 bulk flowables (Xtra-Base and Filtek) was about the same with Xtra-Base ending marginally higher total volumetric shrinkage value. Therefore it can be seen that the two materials (SDR and Venus) with the fastest polymerization rates (highest slopes) also had the largest total volumetric shrinkage. Our shrinkage value obtained for Z250 (1.13%) corresponds well with other published values of ~1.1% [21,33,36-39].

The ratio of the viscous base monomer to the more flowable diluent monomers has also been found to be a large contributing factor to the percentage of polymerization shrinkage [40]. However, in this study the influence that the ratio might have on the volumetric change, could unfortunately not be sensibly discussed as the manufacturers of the dental materials did not provide the exact ratio or percentage of different monomers contained in the dental materials (Table 1). By combining various monomers to create a multifunctional organic matrix - a reduction of polymerization shrinkage and water sorption can be achieved [40].

It was also reported that the higher the molecular weight of a molecule (Table 2) the lower the shrinkage [24-27], but when there are variations in the mixtures of chemicals with different molecular weights and in different ratios (like the flowables tested in this study) it would not be possible to illustrate clear trends.

Despite all the above-mentioned factors which might have varying influences on the speed and volume of shrinkage, this study proved that the only reliable way to establish and compare the performance of the materials is by measuring the volumetric shrinkage.

Conclusion

Differences in the volumetric change amongst all four bulk fill flowable composites were found. However, the technical brochures on the bulk fill flowable composites advocate filling increments of 4mm layers. All the bulk fill flowable composites had a volumetric shrinkage greater than that of the Z250 control. Therefore, it can be concluded that it would be advisable to place layers of 2mm increments.

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