Measuring polymerization shrinkage of composites utilizing a gas pycnometer

Utilização de picnômetro a gás para obtenção da contração de polimerização de resinas compostas

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ABSTRACT

The objective of this laboratory study was to evaluate the volumetric contraction of five resin composites currently in use. A helium gas pycnometer was used to determine the volume of specimens prior to and after photopolymerization from which total volumetric contraction was obtained. The resin was weighed in an analytic balance and inserted into the pycnometer chamber, the volume of which is known, and hermetically sealed. The volume of the specimen was determined by measuring the pressure change of helium when it was opened up to the expansion chamber. In this study, 15 cycles of pressurizing were repeated for volume determination for each specimen. The arithmetic mean volume was obtained. The final volume was evaluated as done before. The percentage contraction (P) was calculated by: $P = 100(SV_i - SV_f) / SV_i$*, where SV is specific volume and the suffixes i and f indicate measurements before and after polymerization, respectively. The measured volumetric shrinkage ranged from 0.56% for Z250 (3M-ESPE) to 3.26% for P60 (3M-ESPE). The gas pycnometry is a promising method and its mechanism should be more explored for investigating dental materials.*

UNITERMS

Resin composite; polymers shrinkage

INTRODUCTION

Resin composites are restorative materials especially coveted for their aesthetic appearance. Although great improvements were introduced in the last decades, many drawbacks relating to these materials are observed. Adhesive and wear resistance, postoperative sensitivity, microleakage and polymerization shrinkage[4] still worry researchers and clinicians.

Polymerization shrinkage is mainly the result of the rearrangement of the molecules into less space than was required for the liquid phase of mobile monomer molecules[2] and it also depends on the filler level and the type of resin used to structure composites[11]. In aesthetic dentistry, this phenomenon is unwelcome once it presents a volume reduction of the material and its dysadaptation in dental cavity walls[15]. Through the gap between the tooth and restoration, oral fluids and essentially bacteria could permeate and generate recurrent caries and postoperative sensitivity[8].

There are two general approaches to determine a material shrinkage: volume dilatometry and non-volume dilatrometric methods[21].

For linear contraction, measurement devices were constructed as illustrated by Wilson[23] in 1978, where a disk-shaped specimen centrally positioned within a brass ring is sandwiched between a glass plate and a thin microscope cover slip. From the deflection of the cover slip, measured by a transducer, the polymerization shrinkage is determined. Sakaguchi et al.[19], explored in 1991, a method for monitoring the polymerization shrinkage of composite resins utilizing electrical resistance strain gauges that are extremely sensitive to linear dimensional changes. In addition, a "linometer" method was described by De Gee et al.[7] (1993). The set up consisted of a contactless displacement transducer, of which the sensor was placed inside a vertically oriented quartz tube. A thin aluminum disk is placed over the sensor; the composite is placed over it, and a glass slide on the open end of the quartz tube. Through the glass slide, the materials are light cured for one minute and the displacement of the aluminum disk caused by the lifting action of the contracting material is registered and the percentage of linear contraction is calculated. The authors believe that the true linear polymerization shrinkage could be obtained for both unfilled resins and composites, independently of the sample geometry. Other complex and extremely sensitive approach was also recently described[10] where a novel laser interferometric method was used. The equipment associates basically a Michelson interferometer and a low-power helium-neon laser unit. The resin composite specimen in sandwiched between two optical flats. One (superior) is fixed, while the other (inferior) is free to move and consists in a second-surface mirror, where the mirrored side is opposite the sample. The linear contraction is a result of the reduction in pathlenght of the laser beam inside the interferometer, when this is pointed to the mirrored optical flat, which displace (is lifted) due to composite adherence during polymerization.

To obtain volumetric shrinkage values, the most commonly used devices are the water[1,14,18] or mercury dilatometer[3]. They are based on the linear height changes of a column of fluid connected to a reservoir surrounding the test substance[2]. The mercury apparatus usually follows the basic pattern used by Smith & Schoonover[20] in 1953 (that is a dilatometer with mercury filled capillary).

Each of these techniques has its advantages and disadvantages. The linometer records dimensional change in just one direction in which the free shrinkage condition is achieved by separating the materials from the aluminum and glass surfaces with grease. Obstruction of contraction movement at these surfaces would enhance the contraction in the axial measuring direction and would exaggerate the shrinkage measurement[7]. The dilatometer records the volumetric change of a material soaked in mercury or in water bath. In water bath, the material may absorb water while undergoing setting, altering the results[1]. Because of the problems of access of the light source, and due to opacity and reflexive characteristics of mercury, it is more difficult for such methods to be applied to light cure dental materials[16]. Also, slight ambient temperature fluctuations lead to significant instability, because of thermal expansion/contraction of the surrounding fluid[5, 7, 22]. In addition, the researcher must take care while handling the mercury device because of its potential health hazards[5].

It is relevant to dentists to distinguish materials that present low shrinkage after polymerization. Although several techniques to diminish the effects of polymerization shrinkage are being described, the knowledge of the properties of resin composites can imply an important support for the professional. The purpose of this work is to evaluate the volumetric polymerization shrinkage of five resin composites currently in use by means of a helium gas pycnometry technique.

MATERIALS AND METHODS

The Multivolume Pycnometer 1305 (Micromeritics - Norcross, USA) is designed to measure rapidly the skeletal volume of powders, granules, or any other solid objects having low vapor pressures and to permit computation of absolute density when weight information is supplied. A skeletal volume is the volume that includes the open pores of the sample but does not include the closed pores (Micromeritics Multivolume 1305 operator's manual). The specimen chamber of this equipment has a volume of 8,162cm^3.

Five commercially available resin composites, presented in Picture 1, were studied in this work.

Each specimen of about 3.5g (one for material) of resin composite was individually weighed in an analytic balance of 0,00001g precision (Analytical Plus-Ohaus, Switzerland), immediately inserted into the pycnometer chamber and then, hermetically sealed. The test was performed at a laboratory room with controlled temperature (23± 2˚C) and humidity (45±5 %); the pycnometer was previously calibrated.

This apparatus operates by detecting the pressure change of pure helium gas resulting from displacement of the gas by a solid object. After sealing, a vacuum (with a pressure of 1atm) was created in the specimen chamber for 20 minutes. After this period, helium gas was flowed through the specimen chamber by five minutes. These steps are recommended by the pycnometer's manufacturer to eliminate any residual vapors (ex: water) that

PICTURE 1 – Tested materials

	Resin composites				
	Durafil VS	**Z100**	**Filtek Z250**	**Filtek P60**	**Surefil**
Shade	A2	A2	A2	A3	A
Mean filler size (µm)	0.04	0.70	0.60	0.60	0.80
Manufacturer	Kulzer, GmBH, Germany	3M-ESPE, St. Paul, MN, USA	3M-ESPE, Paul, MN, USA	3M-ESPE, St. Paul, MN, USA	Dentsply Milford, DE, USA
Batch #	010129	0WA	0EB	0CE	991020

could be present in the specimen chamber or on the surface of the specimen and would interfere with the pressure ratios measured. The specimen chamber was pressurized (purged) with helium to a value P1 (P1= ± 19.5psig) according to pycnometer manufacturer's instructions. The pycnometer has an internal expansion chamber of known volume, which is isolated from the specimen chamber by a valve. When this valve is opened, the pressure of the system is allowed to reach equilibrium, and this resultant value is measured (P2).

The specimen volume (V) was obtained by the following equation:

$$V = \frac{\text{Volume of specimen chamber} - \text{Volume of expansion chamber}}{(P1/P2)-1}$$

In this study, 15 cycles of pressurizing (purges) were repeated for each material volume determination and the arithmetic mean was calculated.

Out of the chamber, each specimen of resin composite was cut into slices of 2mm-thick over a glass plate (about 25 slices) and photopolymerized individually according to manufacturer's directions with the conventional technique. The light pointer was localized next to the material and a visible light-curing unit with halogen lamp (Optilux 2-Gnatus, Ribeirao-Preto, SP, Brazil) was used. The potency of the light source was measured continuously (at the start of polymerization of each material) by a radiometer (Curing radiometer: model 100 Demetron Research Corp.), performing 480 mW/cm². While one slice was being polymerized, the others were covered to protect them from ambient light interference. The same procedure was done after the polymerization of each increment. The amount of increments of each material was weighed again and the final volume was evaluated by the pycnometer as done before.

The percentage of shrinkage (P) was calculated by:

$$P = \frac{100\,(SV_i - SV_f)}{SV_i}.$$

Where the suffixes *i* and *f* indicate the measurements before and after polymerization, respectively. SV_i is initial specific volume, given by $SV_i = volume_i/mass_i$, and SV_f is final specific volume, given by $SV_f = volume_f/mass_f$.

RESULTS

The results obtained are shown in Table 1. The Filtek Z250 composite exhibited the least percentage of shrinkage among the five tested materials and the Filtek P60 exhibited highest.

Table 1 – Comparative values of percentage shrinkage (P) of composites

	Resin composites				
	Durafil VS	**Z100**	**Filtek Z250**	**Filtek P60**	**Surefil**
P*	2.40% (0,2)	1.97%(0,3)	0.56% (0,3)	3.26% (0,4)	1.11% (0,4)

*Standard deviation

DISCUSSION

The dimensional stability of dental composites is essential to the longevity and function of the restoration[5]. The contraction of composites during curing can lead to some clinical problems. Depending on its magnitude, it can cause disruption of the bond (creating gaps) and deflection of the tooth cusps in some types of cavity configuration[18].

Some clinical approaches extensively described in Literature could be useful to control this problem, like placing composites in small increments (incremental technique)[8, 12,15] and the use of a glass-ionomer cement base. Other aspects such as the type of the bonding agent, additional coats of bonding agent and the use of a flowable or a chemical composite base remain being thoroughly studied[4, 12-3]. These techniques were created not just to control the effects of polymerization shrinkage of composites, but also to control the problems associated with the dental cavity configuration, or *C-factor*, an important aspect in restorative dentistry well discussed by Feilzer et al.[9] (1987).

In the present study, the equipment utilized consists in a multivolume helium gas pycnometer. Cook et al.[5] initially introduced this method in 1999. It accomplishes the measurement of skeletal volumes by observing the reduction of gas capacity in the sample chamber caused by the presence of the sample. This instrument does not have active temperature control of the measurement chamber, but employs a large thermal mass to enable passive regulation of the temperature in the measuring chamber and the expansion chamber to less than ±0.01°C. Thus, the temperature is considered constant while measuring is done. Helium is an inert gas and it can penetrate in the surfaces pores of the material whereas mercury and water cannot.

In this work, the volumetric shrinkage of tested materials ranged from 0.56 per cent to 3.26 per cent. Filtek Z250 composite presented the least percentage shrinkage among the five materials examined. According to the manufacturer of the resin composite, this is in part explained by the high molecular weight of the monomer system, which results in less shrinkage. Anyway, for Z250 the percentage shrinkage value was much lower than the value obtained by Nagem Filho[16] (2000), about 2.1 per cent and by Fogleman et al.[10] (2002), 2.11 per cent. Also for Surefil the value was lower than that found by Norling et al.[17] (1999), i.e. 1.9 per cent. Deb[6] (2003) reported for Surefil value of 0,88% of shrinkage using the linear transducer method.

For the composite Z100, which was also tested by Cook[5] (1999) by a gas pycnometer, the percentage shrinkage value (2.12 per cent) was similar to the value obtained in this work (1.97 per cent). Also, comparing to Norling et al.[17] (1999) the results were analogous. In their work, the shrinkage of Z100 was about 1.8 per cent. Fogleman et al.[10] (2002) showed value of 2.32%. The value of shrinkage for P60 composite also was higher than expected. P60 and Z250 composites are materials with similar constitution, according to manufacturer's technical profile. Theoretically, they would have presented also similar volume shrinkage values. The value found in the present work (3.26%) is superior to 1.95% found by Fogleman et al.[10] (2002) that utilized the interferometric laser linear technique.

One of the reasons involving this discrepancy in the obtained results may be related to the different methods (not standardized) to evaluate polymerization shrinkage.

In the present work the vacuum pressure initially created in the equipment chambers to eliminate some vapors or substances in the specimen surface, may interfere on the obtained values. In this work, this possibility is real, essentially because the sample of resin composite was divided for the curing procedure, exposing more the surface area. Although vacuum pressure was applied equally for all materials, one material may release more volatile ingredients than others may and it may be related to the material condition (if it is cured or uncured). This kind of speculation must be more investigated.

While dividing the material for polymerization increments of 2mm-thick were performed for each material. This step was necessary accordingly to composite's manufacturers to achieve their maximum conversion. The 3.5g specimens would not polymerize adequately and the subpolymerization could vary among materials because of their different characteristics and composition. Moreover, the best equipment accuracy according to pycnometer operator's manual is achieved when the volume of the specimen is about 1 to 2/3 of the volume of the chamber. For this reason, the test was not conducted in 2mm specimens from the beginning.

CONCLUSION

The resin composite Filtek Z250 presented the least percentage of volumetric shrinkage and was followed by Surefil, Z100, Durafil VS and Filtek P60, respectively. The gas pycnometry seems to be useful to investigate polymerization shrinkage of resin composites, however, each variable of this technique should be more investigated to confirm your accuracy when measuring resin composites.

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RESUMO

O objetivo deste estudo laboratorial foi analisar a contração volumétrica de polimerização de cinco marcas comerciais de resinas compostas. Um picnômetro a gás foi empregado para determinar o volume dos espécimes antes e após a sua fotopolimerização, de forma que a contração total foi obtida. A resina composta não-polimerizada foi inicialmente pesada em uma balança analítica, inserida na câmara de análise do equipamento (cujo volume é conhecido) e hermeticamente fechada. O volume inicial do espécime foi determinado através da alteração de pressão do gás hélio, quando este é injetado na câmara e depois liberado para expansão em reservatório de volume também conhecido. Neste estudo, 15 ciclos de pressurização foram realizados para a determinação do volume inicial para cada espécime. O valor final foi obtido através da média aritmética dos dados. Fora da câmara, os espécimes foram polimerizados em incrementos e novamente pesados. Para a obtenção do volume final as mesmas etapas anteriormente descritas foram realizadas. A porcentagem de contração (P) foi calculada através da seguinte fórmula: $P = 100(SV_i - SV_f)/ SV_i$, onde SV é o volume específico e os sufixos *i* e *f* indicam as medidas iniciais e finais, respectivamente. A porcentagem de contração obtida para os materiais analisados variou entre 0,56% e 3,26%. Trata-se de uma metodologia promissora, de fácil execução, e seu mecanismo deve ser mais explorado para o estudo do desempenho de materiais odontológicos.

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Resina composta; contração de polimerização

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