

# Polymerization Shrinkage Stress of Composites Photoactivated by Different Light Sources

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The purpose of this study was to compare the polymerization shrinkage stress of composite resins (microfilled, microhybrid and hybrid) photoactivated by quartz-tungsten halogen light (QTH) and light-emitting diode (LED). Glass rods (5.0 mm x 5.0 cm) were fabricated and had one of the surfaces air-abraded with aluminum oxide and coated with a layer of an adhesive system, which was photoactivated with the QTH unit. The glass rods were vertically assembled, in pairs, to a universal testing machine and the composites were applied to the lower rod. The upper rod was placed closer, at 2 mm, and an extensometer was attached to the rods. The 20 composites were polymerized by either QTH (n=10) or LED (n=10) curing units. Polymerization was carried out using 2 devices positioned in opposite sides, which were simultaneously activated for 40 s. Shrinkage stress was analyzed twice: shortly after polymerization ( $t_{40s}$ ) and 10 min later ( $t_{10min}$ ). Data were analyzed statistically by 2-way ANOVA and Tukey's test ( $\alpha=5\%$ ). The shrinkage stress for all composites was higher at  $t_{10min}$  than at  $t_{40s}$ , regardless of the activation source. Microfilled composite resins showed lower shrinkage stress values compared to the other composite resins. For the hybrid and microhybrid composite resins, the light source had no influence on the shrinkage stress, except for microfilled composite at  $t_{10min}$ . It may be concluded that the composition of composite resins is the factor with the strongest influence on shrinkage stress.

Key Words: composite, photoactivation, shrinkage stress, halogen light, LED.

## INTRODUCTION

Polymerization is the chemical reaction that transforms small molecules into large polymer chains or networks. Monomer molecules are at intermolecular distances of 3-4 Å, but when they polymerize, the distance between the so formed polymer units is only 1.5 Å. This accounts for the shrinkage during the polymerization process, typically of the order of 1.5-5% (1). The magnitude of polymerization shrinkage is determined by the number of covalent bonds formed, that is, by the degree of conversion of the double carbon bonds of the monomers, as well as by the size of these molecules.

The larger the molecules, for a same material volume, the smaller the number of bonds established and, thus, the smaller the polymerization shrinkage (2).

In the field of dental composites, different light-curing units (LCU), such as the quartz-tungsten halogen (QTH) lamps and light-emitting diodes (LED), can be used for photoactivation. LCU efficiency depends on the total energy concept. This concept explains that both intensity and photo-initiation time are important for efficient composite polymerization. When adequate curing with short curing time is desired, a higher intensity is required. Higher intensity also means higher polymerization shrinkage stress at the tooth-restoration

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interface, as well as microleakage (3,4).

There are difficulties associated with QTH units, such as expected life span of less than 100 h and the need for using filters due to high heat generation within the quartz bulb (5). The LED-structured polymerization technique has appeared as an alternative to overcome or minimize these shortcomings. LEDs have several advantages over QTH units, namely less heat production, continuous light production even over time, narrow wavelength (470 nm) and complete light beam absorption by camphoroquinone, which is the most common photoinitiator in composite resins (6). New high-power LED devices have recently been developed, and this new technology offers irradiation similar to QTH lamps, with a view to provide higher quality polymerization, and activation of photoinitiators others than camphoroquinone, since some composites have different photoinitiators in their compositions, such as PPD (phenyl propadione) and BAPO (bis-acryl-phosphinoxide) (7).

Factors others than light intensity inherent to the restorative technique are directly related to the polymerization shrinkage in addition to. Factors like light curing modulation, increment size, C-factor, base material, and polymerization kinetics are included (8). As far as the material is concerned, the type and percentage of monomer and filler may determine the degree of cure, the time needed for polymerization, the quality of the polymer links, the shrinkage resulting from the process (9), and the shade and opacity of the composite resin (10).

This study evaluated the polymerization shrinkage stress of 3 types of composite resin polymerized by QTH and LED light-curing units. The tested null hypothesis was that composite shrinkage stress is not influenced by either the type of resin composite or the light source.

## MATERIAL AND METHODS

Three composite resins and one adhesive system were used in this study, as shown in Table 1.

Glass rods (5.0 mm in diameter x 5.0 cm in height) were fabricated and one of the flat ends was subjected to air abrasion with aluminum oxide to provide the surface roughness necessary for further retention of a composite resin increment. Scotchbond Multipurpose adhesive system was applied on the air-abraded flat end and was photoactivated with a QTH light-curing unit for the time recommended by the manufacturer. In order to obtain each specimen, 2 glass rods were assembled to a universal testing machine (EMIC DL-2000; São José dos Pinhais, PR, Brazil) in a vertical position using tensile test claws (Fig. 1A). The distance between the upper and lower rods was standardized in 2 mm. A composite resin increment was placed on the flat end of the lower rod using a hand instrument (Fig. 1B) until filling the 2-mm-high space between the rods. The relationship between bonded and non-bonded faces, corresponding to Factor C, was 2.5.

An extensometer was attached to the glass rods

Table 1. Materials used.

Material	Type	Monomers	Composition		Manufacturer
			Particles size (µm)	Volume (%)	
Heliomolar	Microfilled composite	Bis-GMA, UDMA	0.04 - 0.20	46%	Ivoclar/Vivadent, Schaan, Liechtenstein
Esthet-X	Microhybrid composite	Bis-GMA, Bis-EMA, TEGDMA	1.00 - 0.04	60%	Dentsply Caulk, Milford, DE, USA
Charisma	Hybrid composite	Bis-GMA, TEGDMA	2.00 - 0.04	61%	Heraeus Kulzer, Hanau, Germany
Scotchbond Multipurpose	Adhesive system	-	-	-	3M/ESPE, St. Paul, MN, USA

Bis-GMA, bisphenol A diglycidyl ether dimethacrylate; Bis-EMA, Ethoxylated bisphenol A dimethacrylate, TEGDMA, Triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

in order to measure the shrinkage stress (kgf). The composite resin was photoactivated with 2 light-curing units positioned in opposite sides, perpendicular to the glass rods, at a distance of 5 mm from the composite resin surface, and simultaneously activated for 40 s (Fig. 1C). Twenty specimens were obtained for each composite resin - 10 were photoactivated with the QTH lamp (Ultralux; Dabi Atlante, Ribeirão Preto, SP, Brazil - power density: 480 mW/cm<sup>2</sup>) and 10 with LED unit (Ultraled; Dabi Atlante - power density: 500 mW/cm<sup>2</sup>). The intensity of light emitted was evaluated with a curing radiometer (Demetron Research Corp., Danbury, CT, USA) before specimen photoactivation, also at the distance of 5 mm.

Immediately after polymerization, the shrinkage stress (kgf) was recorded and considered as the shrinkage at  $t_{40s}$ . The shrinkage stress (kgf) was recorded again after 10 min ( $t_{10min}$ ). Along with the shrinkage, there was also an approximation of the glass rods and the extensometer recorded the resulting strain (kgf).

Based on shrinkage stress values obtained at  $t_{40s}$  and  $t_{10min}$ , for each composite resin polymerized with QTH and LED, the stress ( $\zeta = F/area$ ) was calculated in

MPa. Data were analyzed statistically by 2-way ANOVA and Tukey's test at a 5% significance level.

## RESULTS

Table 2 compares the shrinkage stress mean values and standard deviations recorded at 40 s and 10 min for each material polymerized with the light-curing units.

For all composite resins, shrinkage stress was

Table 2. Shrinkage stress mean values and standard deviations at 40 s and 10 min.

Light-curing unit	Composite resin	Mean shrinkage stress (SD)	
		$t_{40s}$	$t_{10min}$
QTH	Microfilled	0.69 (0.06) a	1.44 (0.14) b
	Microhybrid	1.04 (0.06) a	1.51 (0.28) b
	Hybrid	1.18 (0.09) a	1.83 (0.24) b
LED	Microfilled	0.45 (0.06) a	0.93 (0.18) b
	Microhybrid	1.06 (0.18) a	1.73 (0.41) b
	Hybrid	0.96 (0.15) a	1.38 (0.27) b

Different letters in rows ( $t_{40s} \times t_{10min}$ ) indicate statistically significant differences (ANOVA and Tukey's test;  $p < 0.05$ ).

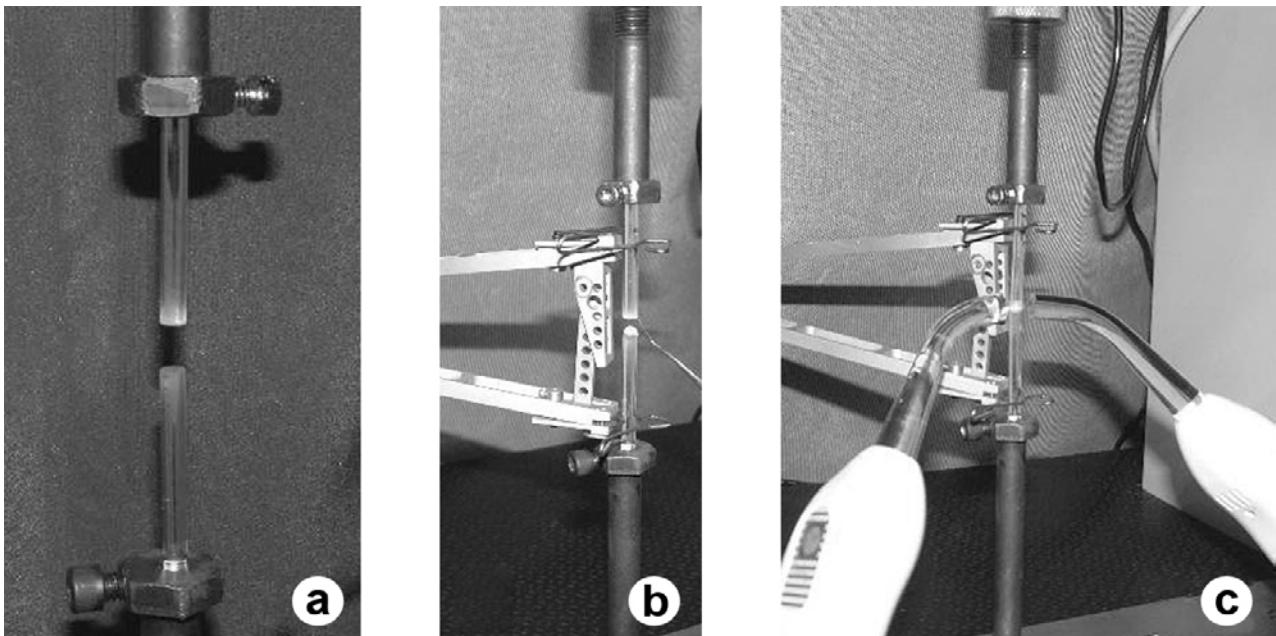


Figure 1. Specimen fabrication. A = glass rods in the testing machine in a vertical position; B = Placement of a composite resin increment on the flat end of the lower rod; C = Simultaneous photoactivation of the composite resin increment.

higher at  $t_{10\text{min}}$ , compared to  $t_{40\text{s}}$ , independent of the polymerizing source, with statistically significant values for each type of composite. Shrinkage stress values were significantly lower ( $p < 0.05$ ) for the microfilled composite resin, followed by microhybrid and hybrid resins. The latter presented stress values for  $t_{40\text{s}}$  similar to those obtained for the microfilled composite at  $t_{10\text{min}}$ , and microhybrid composite at  $t_{40\text{s}}$  and  $t_{10\text{min}}$  ( $p > 0.05$ ).

The microhybrid composite presented a mid-term behavior compared to the other materials. That is, its mean shrinkage stress values were higher than those of microfilled composite resins and lower than those of hybrid composite resins, except for the hybrid composite at  $t_{10\text{min}}$ , which presented significantly lower ( $p < 0.05$ ) mean shrinkage stress when photoactivated by LED.

Figures 2 and 3 present graphically the shrinkage stress mean values and standard deviations recorded at 40 s and 10 min, respectively. The individual behavior analysis for each composite, that is, in terms of the influence of the light-curing unit over the material, showed that at  $t_{40\text{s}}$  (Fig. 2) there was no statistically significant difference ( $p > 0.05$ ) between the light-curing units for hybrid and microhybrid composite resins. There were, however, statistically significant differences ( $p < 0.05$ ) for microfilled composite resins.

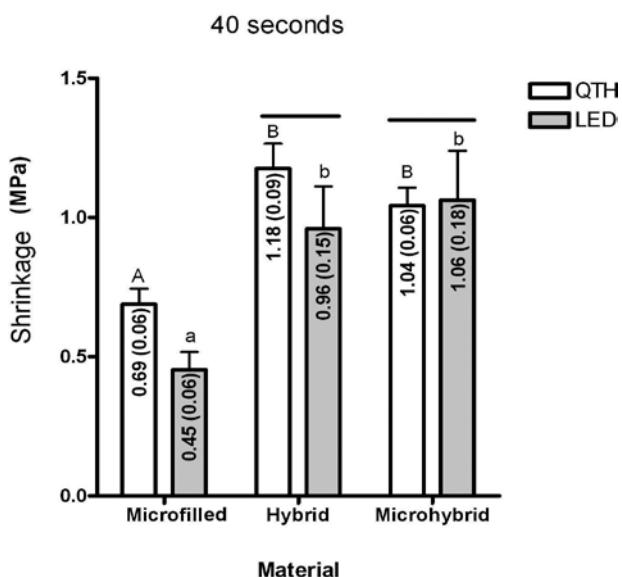


Figure 2. Mean shrinkage stress and standard deviations at 40 s (vertical bars represent standard deviation). Columns under the same horizontal line are not statistically different ( $p > 0.05$ ). Different uppercase letters for QTH and lowercase letters for LED indicate statistically significant differences ( $p < 0.05$ ).

On the other hand, 10 min after polymerization (Fig. 3), shrinkage stress was significantly lower ( $p < 0.05$ ) for the microfilled and hybrid composite resins photoactivated by LED compared to the specimens photoactivated with the QTH lamp.

## DISCUSSION

Shrinkage stress is among the main factors responsible for failures on the adhesive interface and the ensuing clinical failure of composite restorations and the stress magnitude generated during polymerization depends on factors associated with the restorative procedure and the composite (11).

The type of composite photoactivation could interfere on the material's viscous flow. This interference is explained by the polymerization kinetics of composites. During polymerization, composites go through 3 phases referred to as: pre-gel phase (initial polymerization); polymerization phase; and post-gel phase. In the first phase, composites are in the viscoelastic phase and are susceptible to deforming (12). The material presents a low modulus elastic limit, which permits permanent deformation through the sliding of the forming polymeric chains. Volumetric shrinkage in this phase is referred to

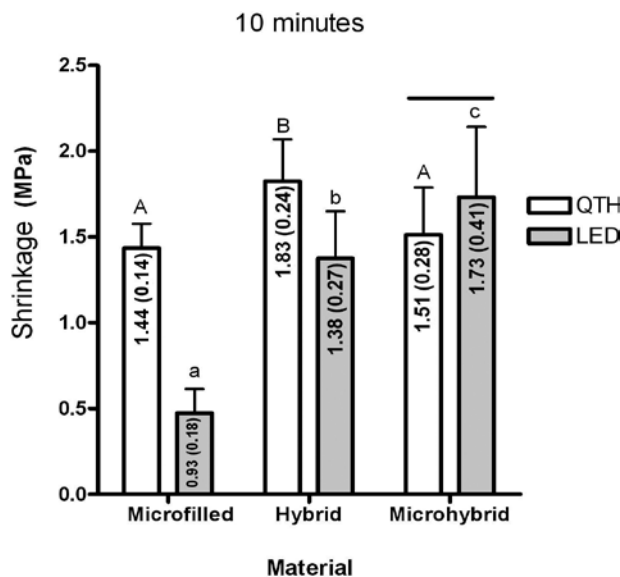


Figure 3. Mean shrinkage stress and standard deviations at 10 min (vertical bars represent standard deviation). Columns under the same horizontal line are not statistically different ( $p > 0.05$ ). Different uppercase letters for QTH and lowercase letters for LED indicate statistically significant differences ( $p < 0.05$ ).



as “pre-gel” or “non-rigid” shrinkage (12).

In the polymerization phase, macromolecules are formed and the macromolecular movement of the organic matrix is inhibited. In this phase, composites no longer tend to deform (13). In the post-polymerization phase, the composites are in a rigid state, but still shrink, though the conversion degree does not change significantly (14). The shrinkage observed in the post-gel phase is clinically relevant, as the material is no longer capable of compensating for contraction by deformation, which results in the development of stresses (15).

Regarding material composition, monomer types and ratio, reaction initiators and inhibitors, as well as the filler quantity are factors that influence elastic modulus and polymerization shrinkage. Volumetric shrinkage is inversely related to filler load. Elastic modulus, on the other hand, is directly related. Therefore, greater filler percentages result in smaller volumetric shrinkages, and greater elastic modulus (15).

Several methods have been developed to determine polymerization shrinkage stress (16). In the present study, the previously described method was used to verify shrinkage stress at 2 moments: shortly after polymerization ( $t_{40s}$ ) and 10 min later ( $t_{10min}$ ). The latter refers to the moment when polymerization shrinkage is completed, since approximately 70-85% of this event occurs immediately after the activation of visible light (17). Hence, after this time, post-gel shrinkage could be analyzed. Results show that shrinkage stress values were higher for  $t_{10min}$ . Previous studies have reached similar results (18). Thus, the incremental technique could be useful for a precise adaptation of the material to the cavity, and permit correct depth of polymerization and good adhesion to the cavity. However, it would not avoid polymerization shrinkage.

This study used Bis-GMA-based composites. The Bis-GMA monomer is a chain with high molecular weight (511) due to the presence of an aromatic ring (19). There is, however, a difference regarding the diluent monomers used in the composition of the composite resins studied.

The UDMA, present in microfilled composites, has a molecular weight of 470. Hybrid composites, on the other hand, have the monomer TEGDMA in their composition, which is formed by a low molecular weight linear chain (19). Microhybrid composites have both Bis-EMA (molecular weight of 452) and TEGDMA as diluent monomers. The composition of these compos-

ites explains the results, which showed that microfilled composites have the smallest shrinkage stress, compared to the other composites. Since its diluent monomer has the highest molecular weight, its polymerization shrinkage was the smallest. Polymerization shrinkage values for hybrid composite resins were very similar to those of microhybrid composite resins, with no statistically significant differences for  $t_{40s}$ . Nevertheless, for  $t_{10min}$ , polymerization shrinkage was smaller, which could be due to the presence of the Bis-EMA monomer, which has a higher molecular weight (19).

Regarding composite resins, shrinkage is largely determined by filler load (20). Monomer volume fraction is inversely related to filler load. Therefore, greater loads incorporated in the material result in smaller monomer volume fraction (18). Consequently, shrinkage will be smaller. This does not apply to microfilled composite resins, due to the presence of pre-polymerized matrix particles in their composition, which reduces the amount of monomers that will shrink during polymerization and provides similar polymerization shrinkage values to those of hybrid composite resins (20). It has been observed, however, that the microfilled composite had the lowest stress values, which is in line with the findings of a previous study (17). The microfilled composite resins, whose inorganic content is 46 vol%, had the lowest polymerization shrinkage compared to the other composites (17).

Studies have shown that using reduced light intensity in the first seconds of photoactivation helps reducing stress values, since it extends the pre-gel phase and permits material flow during the initial moments of polymerization (13). Material flow is a time-dependent property and is therefore influenced by polymerization speed as well. Slower polymerization reactions means that it takes longer to reach the gel-point, thus reaching lower “rigid shrinkage” values (20). Consequently, smaller stress is developed.

The results of the present study showed that light source does not interfere in the polymerization shrinkage of the microhybrid composite resin, which indicates that this type of composite resin can be photoactivated with both light sources (QTH or LED), as observed in previous studies (10,14). Nonetheless, lower shrinkage stress values were obtained with the LED source for microfilled composite resins at either times evaluated and for hybrid composite resins after 10 min. This could be due to the delay in reaction, resulting in more time for composite flow in the pre-gel phase (12,20).

LED devices have less power in the first 10 s of photoactivation, whereas QTH equipments have continuous light. This initial low power density can reduce polymerization reaction speed (12,20), extending the pre-gel phase, and allowing for polymeric chains to rearrange. This would reduce post-gel shrinkage, but with no changes to the composite's conversion degree (6).

Several studies have concluded that energy density, determined by the relationship between power and exposure time ( $\text{mW}/\text{cm}^2 \times \text{seconds} = \text{mJ}/\text{cm}^2$ ), is determinant to composite resin properties (18-20). Low density can interfere on the monomer's degree of conversion and affect its mechanical properties due to the lack of efficiency of light transmission through the composite (7,10). This would cause lower polymerization shrinkage, according to the results of the present study.

The tested null hypothesis could not be accepted. There are several factors that interfere on composite polymerization shrinkage. Among them, material composition appears to be the most important factor regarding this behavior. However, depending on the type of material used, the light-curing unit will also affect the final amount of polymerization shrinkage stress.

## RESUMO

Este estudo comparou a contração de polimerização de resinas compostas fotoativadas por luz halógena (QTH) e diodo emissor de luz (LED). Foram confeccionados bastões de vidro (5,0 mm x 5,0 cm), e uma de suas extremidades sofreu jateamento com óxido de alumínio, sobre a qual foi aplicado um adesivo e fotoativado com luz halógena. Os bastões de vidro foram acoplados verticalmente, em pares, em uma máquina universal de ensaios (EMIC DL-2000) e as resinas compostas aplicadas no bastão inferior. A distância entre os bastões foi padronizada em 2 mm e um extensômetro foi acoplado a eles. As resinas foram fotoativadas ( $n=20$ ), sendo 10 por QTH e 10 por LED utilizando dois aparelhos posicionados em lados opostos, acionados simultaneamente por 40 s. A tensão de contração foi analisada em dois momentos: logo após a polimerização ( $t_{40s}$ ) e 10 min após ( $t_{10min}$ ). A tensão de contração apresentada por todas as resinas foi maior em  $t_{10min}$  do que em  $t_{40s}$ , independente da fonte ativadora. A resina de micropartículas apresentou menores valores de tensão de contração com valores estatisticamente significantes em relação às demais resinas. Para as resinas híbrida e microhíbrida não houve influência da unidade ativadora sobre a tensão de contração, com exceção para a resina de micropartículas em  $t_{10min}$ . Concluiu-se que a composição da resina composta foi o fator que mais interferiu na tensão de contração da resina composta.

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