

## Shrinkage stress of three composites under different polymerization methods

### *Estresse de contração de três resinas compostas sob diferentes métodos de polimerização*

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**ABSTRACT:** The aim of this study was to evaluate the shrinkage stress of three composites under different polymerization methods: halogen conventional polymerization (G1), halogen “soft-start” polymerization (G2) and LED polymerization (G3). The composites tested were Filtek Z-100 (3M/ESPE), Filtek Z-250 (3M/ESPE) and Solitaire 2 (Heraeus Kulzer). For G1, an XL-3000 (3M/ESPE) curing unit with light intensity of 507 mW/cm<sup>2</sup> was employed. In G2, the same light unit was used, but with a reduced light intensity in the first 20 s (166 mW/cm<sup>2</sup>). In G3, an Ultrablue I (DMC) LED curing unit with light intensity of 125 mW/cm<sup>2</sup> was used. The test was performed with a DL 2000 (EMIC) universal testing machine and two metallic molds with a 1 mm space between them. The composites were inserted in the space between the molds and light cured according to the protocols mentioned above. Stress was registered in different periods of time: 10, 20, 40, 60, 90 and 120 s. A significant linear increase of the shrinkage stress over time was observed, except for Z-100 in G2. Generally, LED polymerization (G3) reduced the generated stress when compared to conventional halogen polymerization (G1). In G3, the composite with the additional co-initiator presented lower stress when compared to the other composites tested. The combination between composite and polymerization method produced different patterns of stress behavior. LED polymerization reduced the initial shrinkage stress of the three materials and was influenced by the presence of co-initiators in the composites.

**DESCRIPTORS:** Composite resins; Dental stress analysis; Physical and chemical properties.

**RESUMO:** O objetivo do presente estudo foi avaliar o estresse de contração de três resinas compostas sob diferentes métodos de fotoativação: fotoativação convencional halógena (G1), fotoativação “soft-start” halógena (G2) e fotoativação por LED (G3). As resinas compostas testadas foram a Filtek Z-100 (3M/ESPE), Filtek Z-250 (3M/ESPE) e Solitaire 2 (Heraeus Kulzer). Para G1, um aparelho fotoativador XL-3000 (3M/ESPE) com intensidade de 507 mW/cm<sup>2</sup> foi empregado. Em G2, o mesmo aparelho foi utilizado, mas com a intensidade reduzida nos primeiros 20 s (166 mW/cm<sup>2</sup>); em G3 foi utilizado um fotoativador LED Ultrablue I (DMC) com intensidade de 125 mW/cm<sup>2</sup>. O teste foi realizado com uma máquina de ensaio universal DL 2000 (EMIC) e duas matrizes metálicas com um espaço de 1 mm entre elas. A resina composta foi inserida no espaço entre as matrizes e fotopolimerizada de acordo com o protocolo supracitado. O estresse foi registrado nos diferentes períodos de tempo: 10, 20, 40, 60, 90 e 120 s. Um aumento linear significativo do estresse de contração em relação ao tempo foi observado, exceto para a Z-100 em G2. No geral, a fotoativação por LED (G3) reduziu o estresse gerado em comparação com a fotoativação convencional halógena (G1). Em G3, a resina com co-iniciador na sua composição apresentou menor estresse em comparação com as outras resinas testadas. A combinação entre resina composta e o método de fotoativação produziu diferentes padrões de comportamento do estresse. A polimerização com LED reduziu o estresse de contração inicial nos três materiais e foi influenciada pela presença de co-iniciadores nas resinas compostas.

**DESCRIPTORIOS:** Resinas compostas; Análise do estresse dentário; Propriedades físicas e químicas.

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## INTRODUCTION

Nowadays, one of the determining factors of the polymerization quality is the light power density ( $\text{mW}/\text{cm}^2$ ) produced by the light curing unit (LCU), which represents the amount of photons emitted in the light guide. A minimal power density of  $300 \text{ mW}/\text{cm}^2$  is required to effectively polymerize a 2 mm deep increment with a conventional halogen LCU<sup>6</sup>. During the polymerization reaction, the monomer's Van der Waals double links (C=C) are replaced by nearer covalent links. The global resultant of this phenomenon is a volumetric shrinkage of the material, which may vary from 2 to 5% of the total volume<sup>15</sup>.

Some factors, inherent to the restorative technique, are directly related to the polymerization shrinkage: light intensity, light curing modulation, volume of each increment, C-factor, base material and polymerization kinetics<sup>4</sup>. Concerning the material, 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 and the shrinkage resultant from the process<sup>2,3</sup>.

Light modulation has proven to be an interesting alternative to reduce the stress during composite polymerization. The technique is based on the rationale that the speed of composite polymerization determines the stress generation<sup>9</sup>, and that this speed can be controlled by the initial power density of the LCU<sup>20</sup>.

Recent composites have required less time to be cured, which has probably led to a faster polymerization. Different light intensities and exposure times have been found in literature<sup>8,21</sup>, leading to different behaviors concerning stress generation.

The conventional halogen LCUs, due to their mechanics of light production, emit light in a large band of wavelength, wasting curing energy and producing excessive heat<sup>10</sup>. On the other hand, the LED technology guarantees the production of photons in a very strict wavelength range (between 450 and 490 nm) with a peak of about  $470 \text{ nm}$ <sup>14</sup>. These curing devices, even with lower power densities, have, therefore, proven to be as effective as the conventional halogen LCUs, since their light is all involved in the canphoroquinone absorption band<sup>18</sup>. Besides producing satisfactory mechanical properties in composites<sup>18</sup>, the low light intensity LEDs could also have the same effect on polymerization shrinkage stress as soft-start polymerization. On the other hand, the presence of additional co-initiators with different absorption spectrums could be problematic when the LED LCUs are involved, due to their specific spectrums of light. Little information is found concerning the shrinkage behavior of composites light-cured by LED LCUs.

The aim of the present study was to evaluate *in vitro* the shrinkage stress produced by three composite resins under different polymerization methods over time, testing the null hypothesis that composite resin, source of polymerization and time are not factors influencing the development of stress.

## MATERIAL AND METHOD

The materials employed in the present study and their compositions are shown in Table 1.

**TABLE 1** - Composition of the materials employed in this study.

Composite (Manufacturer)	Filtek Z-250 (3M/ESPE)*	Filtek Z-100 (3M/ESPE)*	Solitaire 2 (Heraeus Kulzer)*
Type	Microhybrid	Microhybrid	Polyglass
Color	A3	A3	A3
Batch #	3WK	3EG	010245
Organic matrix	Bis-GMA, Bis-EMA and UDMA	Bis-GMA and TEGDMA	Ester-metacrylic acid
Filler particle size ( $\mu\text{m}$ )	0.19-3.3	0.01-3.5	1-25
Recommended curing time (s)	20	40	40
Filler loading	77.6% (wt.)	84.5% (wt.)	72% (wt.)
CQ-absorption within 410-500 nm	Y	Y	Y
Co-initiators absorption within < 410 nm	N	N	Y

\*Information provided by the manufacturer. CQ: canphoroquinone; Y: yes; N: no.

The test procedures were executed in ideal laboratory conditions (Temp.: 21.6°C (± 1); Relative Humidity: 58.2% (± 1)). A universal testing machine DL2000 (Emic, São José dos Pinhais, PR, Brazil) was employed for the test. Two identical metallic bars of 50 mm in height, 6 mm in width and 2 mm in thickness were adapted to the machine parallelly with each other. The upper bar was connected to a load cell of 5 kg and the inner bar, fixed on the base of the machine<sup>13</sup>.

A 1 mm space between the bars was established with a digital caliper (Digimatic Caliper – Mitutoyo, Suzano, SP, Brazil - #: BD077206). The composites were inserted with a teflon instrument in the space between the bars using a “U” shaped impression putty as rampart (Impregum – 3M/ESPE, St. Paul, MN, USA 55144 – batch #: 25013).

As demonstrated in Table 2, ten specimens for each composite and light source were made.

The shrinkage stress was recorded since the beginning of the light curing and continued during the following 2 minutes (Mondelli *et al.*<sup>13</sup>, 2003), corresponding to the intervals of 10 s, 20 s, 40 s, 60 s, 90 s and 120 s. The irradiation was executed as near as possible to the composite surface. For G2, the irradiation was executed at 10 mm of distance during the first 20 s. The distance was standardized with a composite stop adapted to the inner bar. After this period, the light guide was placed near to the composite surface. The deformation experienced by the load cell was recorded during 2 minutes and converted in a stress *versus* time graph.

Data was obtained in MPa and submitted to statistical analysis with two- and three-way ANOVA. Additional differences between groups were investigated with Tukey’s test. The confidence level was set at 95% ( $p \leq 0.05$ ).

## RESULTS

The ANOVA test indicated that all three factors evaluated (polymerization method, composite and time) were significant, as well as the interactions between them ( $p < 0.01$ ). In Table 3 the shrinkage tensions (MPa) produced are exhibited and the statistical differences were determined with Tukey intervals ( $p < 0.05$ ).

Generally, all the composites tested showed a significant increase of the shrinkage stress over time. The polymerization method also significantly influenced the behavior of the different composites, in different degrees.

As observed in Table 3 and Graph 1, for the conventional polymerization with halogen light (G1), Z-100 showed the highest stress in the initial period (until 40 s). Z-250 presented the lowest stress at the end of the 120 s. Otherwise, Solitaire 2 presented an initial shrinkage stress similar to that of Z-250, which increased over time, overcoming those of the two other composites.

For G2 (soft-start technique), according to Table 3 and Graph 2, the shrinkage stress over time did not demonstrate a linear increase similar to that observed for the conventional polymerization. Despite the increase in shrinkage stress after the initial period, the stress values for Z-100 at the two final evaluation times were similar to those observed in the first evaluation. Lower stress values were observed for Z-250 in the beginning of the evaluation, and increased more than two times after 120 s. Although an initial lower stress was achieved with Solitaire 2, this material developed the highest stress values in the final evaluation period with this polymerization method.

**TABLE 2** - Description of the different groups evaluated.

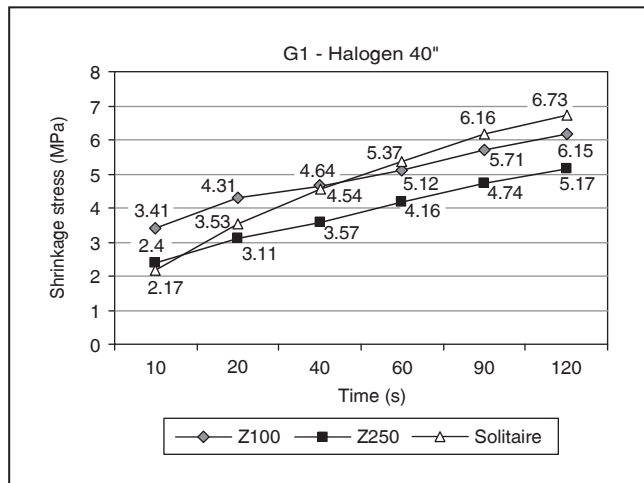
Group	Light source	Power density	Exposure time	Composite	n
G1	Halogen (XL3000 – 3M/ESPE)	507 mW/cm <sup>2</sup>	40 s	Z-250	10
				Z-100	10
				Solitaire 2	10
G2	Halogen Soft-start (XL3000 – 3M/ESPE)	166 mW/cm <sup>2</sup> + 507 mW/cm <sup>2</sup>	20 s + 40 s	Z-250	10
				Z-100	10
				Solitaire 2	10
G3	LED (Ultrablue I – DMC)	125 mW/cm <sup>2</sup>	40 s	Z-250	10
				Z-100	10
				Solitaire 2	10

Power densities were determined with a radiometer Cure Rite 8000 (Efos)(Williamsville, NY, USA) - #: 007517.

**TABLE 3** - Shrinkage tension means (SD) are expressed in MPa for the different conditions tested (composites *versus* polymerization method *versus* time).

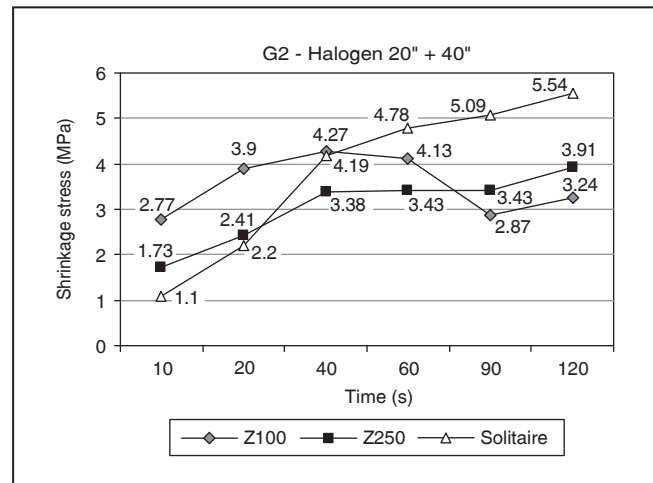
	10 s	20 s	40 s	60 s	90 s	120 s
G1 - Z100	3.41 (0.24) A b ♥	4.31 (0.25) B b ♣	4.64 (0.33) BC b ♣	5.12 (0.35) C b ♣	5.71 (0.40) CD b ♥	6.15 (0.43) D b ♥
G1 - Z250	2.40 (0.11) A a ♣	3.11 (0.14) B a ♣	3.57 (0.13) BC a ♣	4.16 (0.18) C a ♣	4.74 (0.21) CD a ♣	5.17 (0.20) D a ♣
G1 - Solitaire 2	2.17 (0.27) A a ♥	3.53 (0.21) B a ♣	4.54 (0.26) C b ♣	5.37 (0.27) D b ♣	6.16 (0.32) E b ♥	6.73 (0.36) E b ♥
G2 - Z100	2.77 (0.42) A c ♣	3.90 (0.39) B b ♣	4.27 (0.46) B b ♣	4.13 (0.81) B b ♣	2.87 (0.61) A a ♣	3.24 (0.67) AB a ♣
G2 - Z250	1.73 (0.15) A b ♣	2.41 (0.22) A a ♣	3.38 (0.35) B a ♣	3.43 (0.39) B a ♣	3.43 (0.51) B a ♣	3.91 (0.54) B b ♣
G2 - Solitaire 2	1.10 (0.25) A a ♣	2.20 (0.33) B a ♣	4.19 (0.30) C b ♣	4.78 (0.55) CD c ♣	5.09 (0.28) D b ♣	5.54 (0.62) D c ♣
G3 - Z100	1.97 (0.63) A b ♣	3.82 (0.84) B c ♣	4.15 (0.15) BC b ♣	4.58 (0.17) C b ♣♣	5.06 (0.19) CD b ♣	5.39 (0.22) D b ♣
G3 - Z250	1.50 (0.17) A b ♣	2.55 (0.61) B b ♣♣	3.29 (0.38) C a ♣	3.68 (0.35) CD a ♣♣	4.23 (0.41) D a ♣	4.64 (0.42) D a ♣
G3 - Solitaire 2	0.48 (0.17) A a ♣	1.86 (0.18) B a ♣	3.21 (0.21) C a ♣	3.77 (0.23) CD a ♣	4.33 (0.28) D a ♣	4.74 (0.30) D a ♣

Different capital letters are indicating significant differences over time for each composite with each different polymerization method (Tukey value = 0.68). Different minuscule letters are indicating significant differences between composites with each polymerization method (Tukey value = 0.58). Different symbols are indicating significant differences between polymerization methods for each composite tested (Tukey value = 0.59).



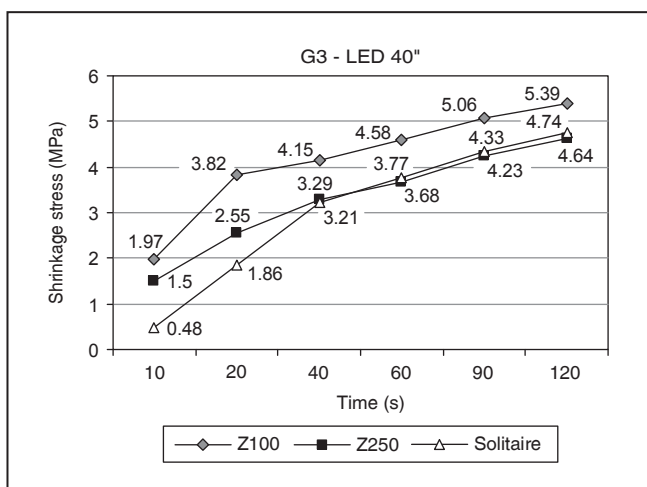
**GRAPH 1** - Comparison of the polymerization shrinkage of the different composites light-cured by halogen light with the conventional technique.

Generally, LED polymerization (G3) reduced the shrinkage stress of the three composites (Graph 3), especially when compared to the conventional polymerization. For all materials polymerized with this method, the stress developed increased until the final evaluation. When light cured with the LED LCU, Solitaire 2 showed the



**GRAPH 2** - Comparison of the polymerization shrinkage of the different composites light-cured by halogen light with the soft-start technique.

lowest stress values in the first two periods, being similar to those of Z-250 in the other periods. Z-100 produced the highest stress values at the end of the evaluation. LED light curing reduced more effectively the shrinkage stress than the soft-start technique in the initial periods for the three composites tested.



**GRAPH 3** - Comparison of the polymerization shrinkage of the different composites light-cured by LED polymerization.

## DISCUSSION

The recent methods described in literature to minimize the effect of the polymerization shrinkage are based on the reduction of the initial light intensity. An increase of the marginal adaptation has been observed by reducing the initial light intensity<sup>12</sup>. The present study showed that the reduction of the light intensity in the first 20 s promoted a significant decrease of the initial shrinkage stress. It also could be observed that polymerization by LED reduced these stresses when compared to halogen conventional polymerization, a result that agrees with the results of previous reports found in literature<sup>8,17</sup>.

All composites continued generating shrinkage forces after interruption of the light exposure, which was already identified in literature as post-gel shrinkage<sup>8,16,17</sup>. Then, the reaction continues occurring with the progressive formation of cross links initiated immediately after the light activation and with the thermal contraction resulting from the exothermic reaction<sup>21</sup>. This was observed in the present study, where most of the groups exhibited increased stress over time.

In G2, an initial light intensity of 166 mW/cm<sup>2</sup> was applied for 20 s, followed by a full intensity of 507 mW/cm<sup>2</sup> for 40 s. This technique promoted a significant reduction of the stress, both in the initial period and at the end of the 120 s. The maintenance of the pre-gel phase for a longer time allows the molecules to modify their arrangement releasing the stress generated during curing<sup>15</sup>. The initial low intensity light exposure is characterized

by the formation of linear polymers, with few cross links, and, thus, more susceptible to movement and structural rearrangement<sup>11</sup>. Braga, Ferracane<sup>4</sup> (2004) pointed out three important factors in the control of the shrinkage stress: the initial light intensity, the exposure time of this reduced light intensity and the time interval between both irradiations.

The use of the LED LCU in G3 reduced the shrinkage stress when compared to G1. In the initial periods this reduction was also higher than that produced by the soft-start technique. The shrinkage stress produced by Solitaire 2 in the initial periods was lower than that of the other composites. This can be explained by the presence of a co-initiator in the material's composition, whose absorption range is lower than 410 nm. Hence, this co-initiator does not participate in the polymerization process when a LED device is employed<sup>19</sup> and probably the result of this study reflects a reduced conversion degree in this composite.

Cavity configuration and the flow capacity of the material are also two important factors in determining the consequences of the composites' shrinkage<sup>7</sup>. In some situations, cohesive failure of the material was observed when the C-factor was too high, between 2.5 and 5.0. In the present study, the C-factor of 1.5 for the specimen volume of 12 mm<sup>3</sup> was maintained constant for all groups.

A variation in the shrinkage tension produced by each composite was observed. It could be justified by the difference in the composition of each material, like the type and percentage of organic matrix<sup>1-3</sup>, filler loading and type and size of particles<sup>1,5</sup>, amount and type of initiator, co-initiator and inhibitor<sup>2</sup>.

The null hypothesis tested in this study was rejected and the three factors evaluated in this study (composite, polymerization method and time) significantly influenced the shrinkage stress produced.

## CONCLUSIONS

Within the limitations of this study, it could be concluded that:

1. Generally, the shrinkage stress of all composites increased during the evaluated time.
2. Concerning the composites, Z-100 presented the highest shrinkage stress in the first periods of time, although, at the end of the evaluated time, Solitaire presented the highest results,

except when cured with the LED LCU.

3. Generally, the polymerization with LED promoted lower shrinkage results.

4. Future studies should be conducted evaluating the degree of conversion of the composites with the same polymerization methods used here.

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Received for publication on Jul 15, 2005

Sent for alterations on Nov 30, 2005

Accepted for publication on Mar 24, 2006