

Polymerization stress, shrinkage and elastic modulus of current low-shrinkage restorative composites

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ABSTRACT

Objective. To compare currently available low-shrinkage composites with others regarding polymerization stress, volumetric shrinkage (total and post-gel), shrinkage rate and elastic modulus.

Methods. Seven BisGMA-based composites (Durafill/DU, Filtek Z250/FZ, Heliomolar/HM, Aelite LS Posterior/AP, Point 4/P4, Filtek Supreme/SU, ELS/EL), a silorane-based (Filtek LS, LS), a urethane-based (Venus Diamond, VD) and one based on a dimethacrylate-derivative of dimer acid (N'Durance, ND) were tested. Polymerization stress was determined in 1-mm high specimens inserted between two PMMA rods attached to a universal testing machine. Total volumetric shrinkage was measured using a mercury dilatometer. Maximum shrinkage rate was used as a parameter of the reaction speed. Post-gel shrinkage was measured using strain-gages. Elastic modulus was obtained by three-point bending. Data were submitted to one-way ANOVA/Tukey test (*p* = 0.05), except for elastic modulus (Kruskal–Wallis).

Results. Composites ranked differently for total and post-gel shrinkage. Among the materials considered as "low-shrinkage" by the respective manufacturers, LS, EL and VD presented low post-gel shrinkage, while AP and ND presented relatively high values. Polymerization stress showed a strong correlation with post-gel shrinkage except for LS, which presented high stress. Elastic modulus and shrinkage rate showed weak relationships with polymerization stress.

Significance. Not all low-shrinkage composites demonstrated reduced polymerization shrinkage. Also, in order to effectively reduce polymerization stress, a low post-gel shrinkage must be associated to a relatively low elastic modulus.

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1. Introduction

Restorative resin composites have been used in dentistry for nearly 40 years [1]. In spite of the undeniable technological advances introduced during these four decades, the volumetric shrinkage that accompanies the chain-growth polymerization of dimethacrylate monomers remains a major concern for the clinical performance of composite restorations. Composite polymerization can be divided in pre- and

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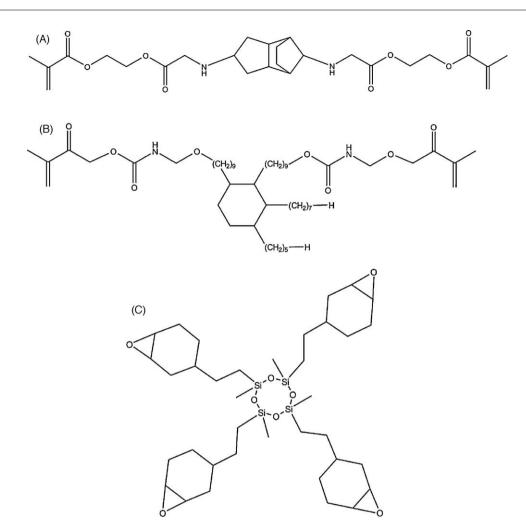


Fig. 1 – Structural formula of base-monomers: TCD-urethane (A), dimer dicarbamate dimethacrylate (B), and silorane (C). Formulas provided by the respective manufacturers.

post-gel phases. In the pre-gel phase, the reactive species present enough mobility to re-arrange and compensate for the volumetric shrinkage without generating significant amounts of internal and interfacial stresses [2–4]. After gelation (postgel phase), the formation of a semi-rigid polymer network hinders plastic deformation [5]. As a consequence, the continued polymerization shrinkage in association with elastic modulus development generates stresses within the material, at the tooth/restoration interface and in the tooth structure [6,7]. This stress state is likely to facilitate gap formation, jeopardizing the longevity of the restoration [8,9]. It must be pointed out that even though a direct relationship between polymerization stress and microleakage has been verified *in vitro* [2,10–12], the deleterious effect of polymerization stress on restoration longevity still lacks clinical evidence [13].

The organic matrix of dental resin composites is formed by a densely crosslinked network, resultant from the co-polymerization of high molecular weight dimethacrylates, such as BisGMA (bisphenol-A glycidyl methacrylate), UDMA (urethane dimethacrylate) and BisEMA (ethoxylated bisphenol-A glycidyl methacrylate), with diluents, such as TEGDMA (triethyleneglycol dimethacrylate). The volumetric shrinkage resultant from the establishment of covalent bonding among methacrylate groups is determined by the monomeric composition, as the higher the concentration of high molecular weight monomers, the lower the amount of carbon double bonds per unit volume [14]. Also, high molecular weight monomers in general present lower mobility, which reduces the final degree of conversion reached by the composite, also contributing to a lower shrinkage [15,16].

Over the years, manufacturers have invested their resources in the development of low-shrinkage restorative composites and, recently, a number of examples of these new materials were made available for clinical use. Some of them are BisGMA-based and use high filler levels or do not contain low-molecular weight dimethacrylates as strategies to reduce polymerization shrinkage. Other materials combine conventional dimethacrylates with new high-molecular weight monomers, for example, tricyclodecane-urethane dimethacrylate (TCD-urethane, Fig. 1A) or dimer dicarbamate dimethacrylate (Fig. 1B).

The TCD-urethane is a low-viscosity monomer that, according to manufacturer's information, would dispense with the use of diluents responsible for the high polymerization shrinkage of BisGMA-based composites. The molecule has three connected rings in its central portion that increase

Material Abbreviation Durafil Dr Heliomolar HM	Filler content			
olar	(vol.%)	Average particle size	Manufacturer	Batch number
	40	0.02-0.07 µm	Heraus Kulzer GmbH, Hanau, Germany	010213
	46	0.04–0.2 µm	Ivoclar Vivadent, Schaan, Liechtenstein	K30118
ELS EL	50	0.07–2.6 µm	Saremco, Rohnacker, Switzerland	04.2012-50
Filtek LS LS	55	0.05–5.0 µm	3M ESPE St Paul, USA	8BF
Filtek Supreme Plus SU	59.5	20 nm (silica), 0.6–1.4 µm (zirconia/silica clusters)	3M ESPE	8PX
(Body)				
Point 4 P4	59	0.4 µm	SDS Kerr, Orange, CA, USA	459692
Filtek Z250 FZ	60	0.19–3.3 µm	3M ESPE	8PF
Venus Diamond VD	64	5–20 µm	Heraus Kulzer	010028
NĭDurance ND	65	40-0.5 µm	Septodont, Louisville, CO, USA	E9810-2
Aelite LS Posterior AP	74	1.1 µm	Bisco, Schamburg, IL, USA	080006817

the flexibility of the monomer backbone and, in theory, would help to accommodate shrinkage. Dimethacrylate-derivatives of dimer acid present higher molecular weight than Bis-GMA and, when associated with other high-molecular weight dimethacrylates, such as BisEMA and UDMA, polymerization stress development would be reduced due to the occurrence of polymer-induced phase separation, i.e., during the reaction, two physically distinct polymeric phases would be formed with different curing kinetics, allowing for more viscous flow during the pre-gel stage [17,18].

In 2007, a silorane-based composite became commercially available [19]. The silorane molecule presents a siloxane core with four oxirane rings attached that open upon polymerization to bond to other monomers (Fig. 1C). The oxirane ring opening causes a volumetric expansion that partially compensates the shrinkage resultant from molecular bonding. Literature data confirmed that a silorane-based commercial composite presented less than 1.0% of total volumetric shrinkage, compared to 2.0–3.5% for BisGMAbased composites [19,20], causing less tooth deflection [21] and microleakage [22,23]. Its mechanical properties are comparable to those of dimethacrylate-based materials [24–26].

As already mentioned, polymerization stress is not determined by volumetric shrinkage alone, but also by composite elastic modulus [10,27]. Reaction rate also plays a role, though evidences show it contributes only marginally [28–30]. Therefore, these new materials should be evaluated in terms of polymerization stress, as well as the other aspects involved in its development, besides shrinkage. There are several reports on the polymerization stress of BisGMA-based composites [10,27,31–33], and it is important to compare new composites with those showing long laboratory and clinical track records.

The purpose of this in vitro study was to compare commercial low-shrinkage with regular composites in terms of polymerization stress, volumetric shrinkage (total and post-gel), elastic modulus and reaction rate. Shrinkage rate was used as an indirect measurement of polymerization rate. The null hypothesis was that results for the low-shrinkage composites are not different from regular composites.

2. Materials and methods

Ten composites were tested, all in A3 shade (Table 1). Seven were BisGMA-based, including a nanofilled (SU), a highlyfilled (AP) and one that does not contain low-molecular weight diluents (LS), and three used monomers alternative to the conventional dimethacrylates. ND contained dimer dicarbamate dimethacrylate, VD utilized a modified urethane (TCD-urethane), and LS was silorane-based. EL, AP, LS, ND and VD are considered low-shrinkage composites by the respective manufacturers.

2.1. Polymerization stress measurements

Poly(methyl methacrylate) rods, 5 mm in diameter and 13 or 28 mm in length, had one of their flat surfaces sand-

Table 2 – Means and standard deviations for polymerization stress, post-gel and total volumetric shrinkage, flexural modulus, and maximum rate of shrinkage. In the same column, means followed by the same superscript indicate absence of statistically significant difference (p > 0.05).

Composite	Polymerization stress (MPa)	Post-gel volumetric shrinkage (%)	Total volumetric shrinkage (%)	Flexural modulus (GPa)	Maximum shrinkage rate (% s ⁻¹)
ND	4.6 (0.5) ^A	0.65 (0.02) ^A	2.4 (0.04) ^B	4.6 (0.3) ^E	0.19 (0.01) ^B
LS	4.3 (0.3) ^A	0.38 (0.02) ^{DE}	1.4 (0.02) ^F	6.8 (0.5) ^B	0.13 (0.01) ^{CD}
P4	4.3 (0.4) ^A	0.67 (0.03) ^A	3.1 (0.02) ^A	4.4 (0.5) ^F	0.28 (0.03) ^A
SU	4.2 (0.4) ^A	0.64 (0.07) ^A	2.0 (0.04) ^{CD}	6.0 (0.7) ^C	0.14 (0.01) ^C
AP	3.4 (0.2) ^B	0.51 (0.04) ^{BC}	2.0 (0.13) ^{CD}	9.3 (0.7) ^A	0.13 (0.01) ^{CD}
FZ	3.3 (0.2) ^{BC}	0.52 (0.04) ^B	1.7 (0.07) ^E	5.6 (0.6) ^D	0.14 (0.01) ^{CD}
VD	2.8 (0.4) ^{BC}	0.39 (0.03) ^{DE}	1.8 (0.03) ^E	4.5 (0.3) ^{EF}	0.13 (0.01) ^{CD}
HM	2.8 (0.4) ^{BC}	0.43 (0.02) ^{CD}	1.6 (0.03) ^E	3.1 (0.3) ^G	0.11 (0.01) ^D
EL	2.7 (0.3) ^C	0.35 (0.02) ^E	2.1 (0.08) ^C	2.0 (0.2) ^H	0.16 (0.01) ^C
DF	2.6 (0.3) ^C	0.43 (0.03) ^{CD}	1.9 (0.03) ^D	1.4 (0.1) ^H	0.14 (0.01) ^{CD}

blasted with 250 μ m alumina. On the shorter rod, in order to allow for the highest possible light transmission during photoactivation, the opposite surface was polished with silicon carbide sandpaper (600, 1200, and 2000 grit) and felt disks with 1 μ m alumina paste (Alumina 3, ATM, Altenkirchen, Germany). The sandblasted surfaces received a layer of methyl methacrylate (JET Acrílico Auto Polimerizante, Artigos Odontológicos Clássico, São Paulo, Brazil) followed by two thin layers of unfilled resin (LS System Adhesive for LS or Scotchbond Multi-purpose Plus, bottle 3, for the other tested composites, both from 3 M ESPE). The unfilled resin was light-cured with a radiant exposure of 12 J/cm² (400 mW/cm² × 30 s).

The rods were attached to the opposing clamps of a universal testing machine (Instron 5565, Canton, MA, USA) with the treated surfaces facing each other with a gap of 1mm. The composite was inserted into the gap and shaped into a cylinder following the perimeter of the rods. An extensometer (0.1 µm resolution) was attached to the rods (model 2630-101, Instron) for the purpose of monitoring the specimen height and providing feedback to the testing machine in order to keep the height constant. Therefore, the value registered by the load cell corresponded to the force necessary to counteract the polymerization shrinkage force to maintain the specimen's initial height. The short rod was attached to the testing machine through a hollow stainless steel fixture with a lateral slot that allowed the tip of the light guide of a quartz-tungsten-halogen unit (VIP Junior, Bisco, Schaumburg, IL, USA) to be positioned in contact with the polished surface of the rod. In order to increase the irradiance output, a turbo tip (7 mm in diameter) was used. The irradiance effectively reaching the composite was estimated by interposing a 13-mm rod between the light tip and the sensor of a dental radiometer (model 100, Demetron Res. Corp., Orange, CA, USA). The reading was multiplied by 1.96 to account for the fact that the diameter of the rod was smaller than that of the sensor (7 mm). Radiant exposure was set at approximately 18 J/cm^2 (570 mW/cm² × 32 s) for all the composites tested. Force development was monitored for 5 min from the beginning of photoactivation and nominal stress was calculated by dividing the maximum force value by the cross-section of the rod. Five specimens were tested for each of the ten composites.

2.2. Post-gel shrinkage measurements

Composite post-gel volumetric shrinkage was determined using strain gages, as previously described in detail [34]. Briefly, a small amount of composite was shaped into a hemisphere, placed on top of a biaxial strain gage and light-cured using a quartz-tungsten-halogen (QTH) unit (XL2500, 3M ESPE) with the light tip placed 1 mm distant from the surface of the composite. Again, radiant exposure was set at 18 J/cm^2 (600 mW/cm² × 30 s). Microstrain resultant from polymerization shrinkage was monitored for 5 min from the beginning of photoactivation in two perpendicular directions. The microstrain values registered in both directions were averaged, given that the materials present homogeneous and isotropic properties on a large scale. This average value was converted to percentage and multiplied by three to represent the volumetric shrinkage. Five specimens were tested for each composite.

2.3. Total volumetric shrinkage determination

Composite total shrinkage was measured in a mercury dilatometer (ADA Health Foundation, Gaithersburg, MD, USA). Approximately 0.1 g of composite was placed on a sandblasted and silanized glass slide. A glass column was clamped to the glass slide, filled with mercury and a LVDT probe (linear variable differential transducer) was placed on top of the mercury column. The composite was light-cured from underneath, through the glass slide using a QTH unit (QHL75, Dentsply) with a radiant exposure of 18 J/cm². The irradiance loss through the glass slide was minimal (600 mW/cm² \times 30 s). Volumetric shrinkage was calculated using the LVDT probe readings and previously recorded mass and density values. Three specimens were tested for each composite. In order to make correlations with polymerization stress values more meaningful, shrinkage data recorded at 5 min were used in the statistical analysis. Maximum rate of shrinkage development was calculated from the first derivative of the shrinkage vs. time curve and was used as a measure of the reaction speed.

2.4. Flexural modulus determination

Specimens $12 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$ (n = 10) were made using a split steel mould. Ten minutes after photoactivation (18 J/cm²),

the specimen was removed from the mould and subjected to three-point bending in a universal testing machine (Q-Test TM, MTS Systems Corp., NC, USA), with 10 mm distance between the supports and cross-head speed of 0.5 mm/min. Based on the linear portion of the load × displacement curve, flexural modulus was calculated according to the following formula:

$$M_{\rm f} = \frac{L \times D^3}{4 \times w \times h^3 \times d} \times 10^{-3}$$

where M_f is the flexural modulus (GPa), *L* is the load recorded (N), *D* is the span between the supports, *w* is the width of the specimen, *h* is the height of the specimen and *d* is the deflection corresponding to *L* (all in mm).

2.5. Statistical analyses

Polymerization stress, volumetric shrinkage (total and postgel) and maximum shrinkage rate data were analyzed using one-way ANOVA/Tukey test. Flexural modulus data were analyzed using Kruskal–Wallis due to the lack of homocedasticity. In both tests, the pre-set global significance level was 5%. Regression analyses were performed with polymerization stress as the dependent variable and total shrinkage, postgel shrinkage, elastic modulus or maximum shrinkage rate as independent variables. Regression analyses using filler content as independent variable were also performed.

3. Results

Table 2 presents the means and standard deviations for polymerization stress, total and post-gel shrinkage, flexural modulus and maximum shrinkage rate. Statistical analysis revealed three sub-sets for polymerization stress results. ND, LS, P4 and SU produced the highest values. AP, FZ, VD and HM formed the intermediate sub-set. The last three were statistically similar to EL and DF.

Post-gel shrinkage varied between 0.35 and 0.67%. P4, ND and SU presented the highest values, all statistically similar. VD, LS and EL presented the lowest post-gel shrinkage. Total shrinkage varied between 1.4 and 3.1%. P4 had the highest shrinkage, followed by ND. EL, SU and AP presented intermediate, statistically similar values, while DF was similar to the latter two. At the low end of the range, FZ, VD and HM presented similar total shrinkage values, only higher than LS. P4 presented the highest shrinkage rate, followed by ND. All the other composites presented statistically similar shrinkage rates except for HM, with a statistically lower average than EL and SU.

Composites displayed a wide range of flexural moduli, between 1.4 and 9.3 GPa. AP presented the highest value followed, in decreasing order, by LS, SU and FZ, all of which were statistically different. ND and VD were statistically similar and the latter was similar to P4. HM showed flexural modulus higher than DF and EL, which presented the lowest values among the composites tested.

Regression analysis revealed no correlation between polymerization stress and total shrinkage ($R^2 = 0.036$). On the other hand, when stress was plotted against post-gel shrinkage, the regression coefficient was 0.458 (Fig. 2). It is noteworthy

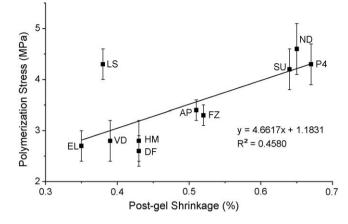


Fig. 2 – Regression analysis between polymerization stress (MPa) and post-gel volumetric shrinkage (%).

that when LS was excluded from the regression analysis, the R² value increased to 0.915. Polymerization stress showed no correlations with flexural modulus ($R^2 = 0.144$) or maximum shrinkage rate ($R^2 = 0.159$). Regression analyses showed no correlation between filler content and total shrinkage ($R^2 = 0.066$), post-gel shrinkage ($R^2 = 0.083$), polymerization stress ($R^2 = 0.113$) and maximum shrinkage rate ($R^2 = 0.103$). A good correlation was observed between filler content and flexural modulus ($R^2 = 0.624$).

4. Discussion

The null hypothesis cannot be rejected because, overall, the composites considered as low-shrinkage presented polymerization stress and its determinants within the same range as those obtained by the regular composites. Specifically regarding post-gel shrinkage, the only exception was EL which, in fact, presented the lowest value found in this study. VD and LS also presented low post-gel shrinkage, but similar to those shown by the microfilled composites (HM and DF). AP and ND, however, developed post-gel shrinkage similar to the other microhybrid composites.

Correlating final flexural modulus and shrinkage values with polymerization stress values is a valid, albeit simplified approach. The changes in composite viscoelastic behavior that occur during polymerization, from predominantly viscous to mostly elastic, make polymerization stress development a quite complex event. Though the relative contributions to stress of shrinkage and elastic modulus are not well defined at this point, the results of the present study indicate that a low volumetric shrinkage does not necessarily correspond to a low polymerization stress development. For example, the high initial flexural modulus shown by LS, also reported previously [19], may explain its high polymerization stress value, in spite of the low volumetric shrinkage (both post-gel and total). In fact, the behavior of the silorane-based composite set it apart from the dimethacrylate-based composites tested, which was made clear by the regression coefficients of stress vs. post-gel shrinkage with (0.458) and without LS (0.915).

AP, on the other hand, showed higher flexural modulus and post-gel shrinkage than LS (27 and 25%, respectively) and 21% lower stress. It could be speculated that the high flexural modulus for AP is largely due to its increased filler fraction, while for LS the highly crosslinked polymer originating from the multifunctional silorane monomer reduces the occurrence of viscous flow. The fact that the flexural modulus of LS is higher than those shown by dimethacrylate composites with similar filler levels suggests a more significant influence of the organic matrix on composite stiffness. The literature on silorane-based composites is controversial. While there are studies showing inferior marginal adaptation [34] and bond strength [35], others reported that restorations using LS caused less tooth flexure [21] and microleakage [22,23] than dimethacrylate-based controls. The present findings support the idea that reduced shrinkage per se does not guarantee interfacial integrity to the restoration.

For AP, the results suggest that the addition of high filler levels to reduce resin volume is not an efficient approach to reduce post-gel shrinkage and polymerization stress. For both variables, the values obtained by AP were statistically similar to the less filled FZ. A possible explanation is that FZ, besides BisGMA, contains BisEMA and UDMA replacing most of the TEGDMA [35]. Reducing the TEGDMA content and replacing it with larger monomers should reduce matrix shrinkage in comparison to AP, which contains a higher concentration of low molecular weight monomers. The polymerization stress of FZ and AP has been compared in two previous studies. The first one, used a similar testing set up, except for the rod material (glass instead of acrylic), and found statistically higher stress for AP, with no significant effect on microleakage [12]. The second study reported statistically higher stress for FZ. However, specimen dimensions, geometry and curing conditions were different, which may have affected the degree of conversion of both materials to different extents [36].

VD and EL presented low post-gel shrinkage and elastic modulus, which can explain their low polymerization stress. According to the respective manufacturers, these materials do not contain low molecular weight diluents, which are usually employed to reduce the viscosity and increase the molecular mobility of the organic matrix [37,38]. By doing so, its glass transition temperature is reduced and higher degrees of conversion can be achieved prior to vitrification [16]. Hence, it is possible that the low-shrinkage and elastic modulus shown by VD and EL, besides a lower concentration of carbon double bonds, may be the result of a lower degree of conversion and a less crosslinked polymer. This is likely to be true for VD, considering that its elastic modulus is low for its elevated filler fraction. EL has shown a relatively low degree of conversion in previous studies [39,40], which in association with its fairly low filler content would explain the low elastic modulus [15].

ND presented high shrinkage and, even considering its low elastic modulus relative to its high filler fraction, developed high stress values. The low elastic modulus is explained by the low crosslink density of the dimethacrylate derivatives of the dimer acids, resulting in a more flexible polymer [17]. However, the high shrinkage was unexpected. The composite contains a high molecular weight base-monomer (847 g/mol), and according to the manufacturer, the dimer dicarbamate dimethacrylate in association with BisEMA and UDMA would result in polymer-induced phase separation. When miscible monomers are not totally compatible in the polymerized state, two separate phases with different reaction kinetics are formed. The phase polymerizing faster remains involved in a less reticulated polymer, allowing for higher conversion and lower shrinkage [18]. Apparently, this mechanism and the absence of low molecular weight monomers were not capable of reducing shrinkage and stress.

Two of the composites showing the highest shrinkage rate (P4 and ND) also presented the highest polymerization stress. However, the other two composites with high stress levels (LS and SU) presented rates statistically similar to most of the remaining materials. Apparently, the other variables exert a more important influence on polymerization stress development than reaction rate, as suggested by previous investigations [28,29].

Post-gel shrinkage values represented only 17-32% of the total shrinkage. In spite of the fact that these two variables were measured using different methods, the results indicate that the majority of the shrinkage takes place during the pre-gel phase, thus limiting stress buildup, and that is in agreement with a previous study [34]. Regression analysis revealed a somewhat weak correlation between total and post-gel shrinkage ($R^2 = 0.480$). Polymerization stress showed a strong correlation with post-gel and no correlation with total shrinkage suggesting that, for materials with dissimilar organic and inorganic contents, differences in reaction kinetics and polymer structure affect their viscoelastic behavior and conversion reached at vitrification. This finding also adds evidence to the fact that the shrinkage fraction occurring prior to vitrification has little effect on stress development. Interestingly, for a group of experimental composites with similar organic matrix and the same filler content, a strong correlation between total shrinkage and polymerization stress has been observed [37].

Polymerization stress results obtained in experimental set ups similar to that used in this study showed a good correlation with microleakage [10–12] and cuspal deflection [41]. However, it is important to emphasize that polymerization stress is a local physical state, not a basic property and, as such, its value is dependent upon geometry and boundary conditions [6]. Within the limitations of this in vitro study, it was possible to conclude that some of the approaches utilized by different manufacturers were able to successfully reduce composite post-gel shrinkage. However, in order to effectively reduce polymerization shrinkage stress, the role of the elastic modulus must be considered as well.

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