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Relaxation mechanisms in low-stress polymer networks with alternative chemistries

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Abstract

Background.—Low-stress resin-based composites (RBCs) are available to the clinician, some using stress relaxation mechanisms on the basis of network reconfiguration, modulated photopolymerization, or chain transfer reactions. This study investigated those materials in terms of their overall stress relaxation and their relationship with polymerization kinetics and compared them with an experimental low-stress thiourethane (TU) material.

Methods.—Experimental composites (bisphenol-A-diglycidyl dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate [50:30:20 mass ratio]; 70% barium aluminosilicate filler; camphoroquinone, ethyl-4-dimethylaminobenzoate, and 2,6-di-tert-butyl-4-methylphenol [0.2:0.8:0.2% by mass]) with or without TU oligomer (synthesized in-house) and commercial composites (SureFil SDR Flow+ Posterior Bulk Fill Flowable Base [SDR Flow+] [Dentsply Sirona], Filtek Bulk Fill Posterior Restorative [3M ESPE], and Filtek Supreme Ultra Universal Restorative [3M ESPE]) were tested. Polymerization kinetics (near-infrared) and polymerization stress (Bioman) were evaluated during light-emitting diode photoactivation at 100 mW/cm^2 for 20 seconds. Stress relaxation was assessed using dynamic mechanical analysis. Data were analyzed with a 1-way analysis of variance and Tukey test ($\alpha = 0.05$).

Results.—The kinetic profiles of all materials differed substantially, including more than a 2-fold difference in the rate of polymerization between TU-modified composites and SDR Flow+. TU-modified RBCs also showed more than a 2-fold higher conversion at the onset of deceleration vs the experimental control and commercial materials. RBCs that used stress reduction mechanisms showed at least a 34% reduction in polymerization stress compared with the controls and

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Disclosures
None of the authors reported any disclosures.

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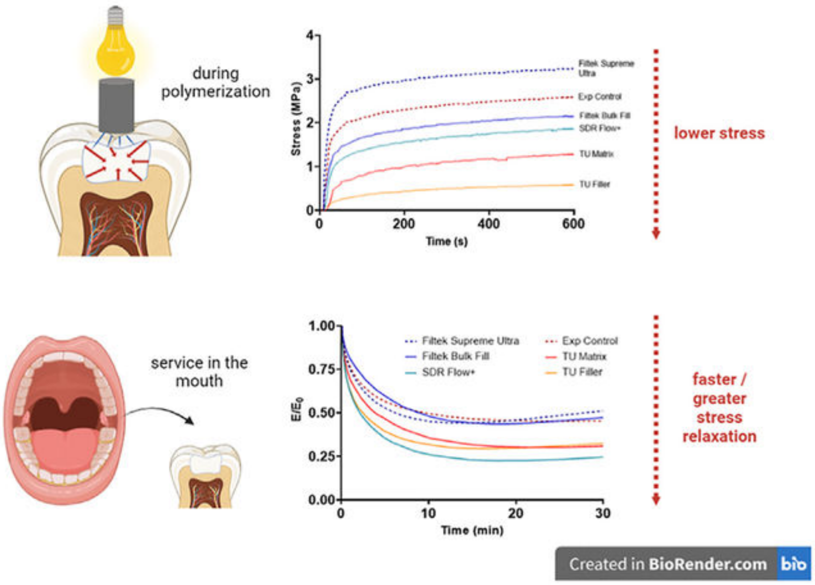
significantly reduced the amount of early-onset stress buildup. SDR Flow+ and the TU-modified RBCs showed the greatest amount of viscoelastic stress relaxation postpolymerization.

Conclusions.—The novel TU-modified materials showed similar or improved performance compared with commercial low-stress RBCs, showing that chain transfer may be a promising strategy for stress reduction, both during polymerization and after polymerization.

Graphical Abstract



Keywords

Resin composites; polymerization stress; stress relaxation; polymerization kinetics

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Introduction

Despite advances in dental composite technology over the past several decades, the performance and clinical life span of resin-based composites (RBCs) are still not optimal.[1] Fundamentally, the photopolymerization process and associated shrinkage strain produce a substantial buildup of stresses within the RBC, particularly at the resin-filler interface, in which the stress concentrates because of modulus differences between the 2 phases,[2] contributing to the relatively short life span of these restorations.[3–5] Numerous strategies have been adopted to mitigate stress in composites, including developing monomers with unique chemistries capable of relieving stress during polymer network formation or enhanced viscoelastic stress relaxation in postcured composites.[6–8] The incorporation of allyl sulfide moieties with methacrylate monomers has resulted in decreased stress through addition-fragmentation chain transfer, a radical-mediated process that occurs during polymerization and promotes network reconfiguration without reducing cross-link density.[9,10] This technology has been incorporated into at least 1 commercial material (Filtek Bulk Fill Posterior Restorative [Filtek Bulk Fill]; 3M-ESPE).

Another promising avenue for reducing polymerization shrinkage stress in commercial RBCs has been shown through the introduction of polymerizable stable radical moieties into the dimethacrylate monomer structure.[11] One commercial example (SureFil SDR Flow+ Posterior Bulk Fill Flowable Base [SDR Flow+] [Dentsply Sirona] used as a bulk fill flowable composite) used this concept to develop a urethane dimethacrylate analog which, when formulated in conjunction with traditional monomers and fillers, provided enhanced polymerization stress reduction compared with conventional composites.[12] The mechanism enables the stabilizing radical group to act as a photomodulator, providing conformational flexibility during polymerization, likely leading to delayed gelation, thus reducing the magnitude of stress that develops within the system.[11]

Thiourethane (TU) oligomers have been used in experimental resins and composites to reduce polymerization stress, promote postpolymerization stress relaxation, and improve fracture toughness.[13–15] Excess thiol functionalities on the TU molecule facilitate chain transfer reactions to methacrylates in the resin, which delay gelation or vitrification and serve as a stress reduction mechanism.[16] The oligomer can be used either as a prepolymer matrix additive or can be covalently tethered to the filler particle surface through methoxy-silane coupling with the goal of reducing stress by targeting the resin-filler interface.[17] Furthermore, it has been shown that bulk TUs can act as covalent adaptable networks via dynamic reactions such as thiol-TU exchange or disulfide exchange.[18–20] Under specific conditions, these reactions can occur in cross-linked networks at room temperature,[18,21,22] and this can be potentially extrapolated to explain the dramatic shrinkage stress reductions seen in prior studies involving TU oligomers.[14,15] The motivation for our study was to try to elucidate the mechanisms that led to the observed increase in fracture toughness that accompanied stress reduction with TU-modified materials because the previous results cannot be explained by the toughening of the more flexible TU bonds.[23] The overall goal is to gain a deeper understanding of the structure of TU-modified polymer networks using well-established stress relaxation techniques in dynamic mechanical analysis compared with commercial materials.

Given the demand for high-performance, low-stress-producing dental restorative materials, this study aimed to evaluate 2 commercial and 2 experimental RBCs designed with alternative chemistries targeting stress reduction. The stress reduction mechanisms for 1 of the commercial materials are based on addition-fragmentation chain transfer–mediated network reconfiguration, the second commercial material is based on intrinsically modulated photopolymerization, and the experimental materials are based on thiol chain transfer reactions. The tested hypotheses were that compared with the controls, the addition of TU would lead to stress reduction in the experimental materials that were similar to or greater than the reduction observed in the commercial low-stress materials.

Methods

TU oligomer synthesis and filler particle functionalization

TU oligomers were synthesized following a previously established protocol developed by Bacchi et al.[16] TUs containing pendant silane functionality were synthesized using a slightly modified protocol, also reported previously[24] and used to functionalize barium aluminosilicate (BAS) (0.7 µm average particle size; Specialty Glass) under acidic conditions, following established protocols.[24–26] The same procedure, with 3-(trimethoxysilyl)propyl methacrylate substituted as the silane moiety, was used to produce methacrylate-functionalized filler particles, which were used in the control formulation described in the following section.

Composite composition

Experimental composites were prepared using bisphenol-A-diglycidyl dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate (BUT) (50:30:20 mass ratio; Esstech), camphorquinone and ethyl-4-dimethylaminobenzoate at 0.2 and 0.8 wt%, respectively and butylated hydroxytoluene at 0.2 wt%. The inorganic filler content was 70 wt% (silanized BAS/fumed silica at 95:5 mass ratio, ~40 nm; Evonik Industries). Three experimental composites were tested: experimental control (BUT matrix, methacrylate-silanized BAS), TU matrix (80 wt% BUT + 20 wt% TU, methacrylate-silanized BAS), and TU filler (100 wt% BUT matrix, TU-silanized BAS). In addition, 3 commercial composites were used as recommended by the manufacturer: Filtek Supreme Ultra Universal Restorative (Filtek Supreme Ultra) (3M ESPE) (commercial control), Filtek Bulk Fill, and SDR Flow+. These materials and compositions are outlined in Table 1.

Photopolymerization kinetics and degree of conversion (DC)

A light-emitting diode curing light (DEMI Plus; Kerr Dental) was used for all photopolymerization experiments. The maximum irradiance of the curing light was 610 mW/cm^2, measured using an external thermopile power meter (Molectron PM 5200; Coherent Inc). The kinetics of polymerization were measured using real-time near-infrared spectroscopy (n = 3) (Nicolet 6700; ThermoFisher Scientific). Specimens 10-mm diameter × 0.8-mm thick were photocured between glass slides for 20 seconds at an effective irradiance of 100 mW/cm^2 (radiant exposure of 2 J/cm^2) for this experimental setup. The area of the methacrylate absorbance peak at 6,165 cm^{-1} was monitored for 180 seconds, and the DC was calculated on the basis of the change in peak area.[27] The maximum rate of polymerization (Rp_{max}) was calculated as the maximum value of the first derivative of the conversion vs the time profile.[28] The DC at which Rp_{max} was registered was used as a proxy of the onset of deceleration.[28] The infrared setup for the kinetics experiments limited the positioning of the light guide of the photocuring unit in such a way that resulted in a low irradiance effectively reaching the surface of the specimen. Recognizing this irradiance could be considered low for the clinical situation; additional static conversion measurements were conducted at higher radiant exposure for specimens of the same geometry (n = 3; 610 mW/cm^2, 20 seconds per side, 24 J/cm^2).

Polymerization stress

Polymerization stress development was measured in real-time using a high-compliance cantilever beam-based Bioman system,[29] developed and validated in a previous article.[30] Briefly, 0.8-mm thick composite specimens were formed between a silica glass slide treated with silane (Ceramic Primer; 3M ESPE) and a 5-mm diameter steel piston treated with metal primer (Z-Prime Plus; Bisco Inc). The specimen was polymerized through the glass slide for 20 seconds (irradiance = 100 mW/cm^2; radiant exposure = 2 J/cm^2). Force data were collected for 600 seconds; polymerization stress was calculated and plotted as a function of time (n = 5).[30]

Stress relaxation

Silicone molds situated between glass slides were used to create composite bar specimens (1 × 3 × 25 mm), photocured for 90 seconds per side (light-emitting diode at 610 mW/cm^2) and subsequently thermally cured for 24 hours at 180 °C to high conversion (>90%) to prevent additional polymerization during stress relaxation testing. The requirement to eliminate the potential for postcuring is a limitation of the test and likely underestimates the potential stress relaxation. Dynamic mechanical analysis was used to measure temperature-dependent viscoelastic stress relaxation (Q800 Dynamic Mechanical Analyzer [DMA]; TA Instruments). Three specimens were subjected to a fixed 0.05% tensile strain for 30 minutes at discrete temperatures ranging from 80 to 155 °C at 15 °C increments, whereas the DMA recorded the relaxation modulus. The time point at which the relaxation modulus was reduced by 50% was defined as the characteristic relaxation time. These experiments also allow for the elastic modulus of each material to be obtained from the stress relaxation curves.

Statistical analysis

Normality (Shapiro-Wilk test) and homocedasticity (Bartlett or Levene test) were tested. Data were analyzed with a 1-way analysis of variance and Tukey multiple comparisons test. Paired *t* test analyses were used to compare DC for groups irradiated with 2 or 24 J/cm^2 (α = 0.05).

Results

All data were normally distributed and homocedastic.

Photopolymerization reaction kinetics and DC

The DC at both radiant exposures, Rp_{max} and DC at Rp_{max}, for all groups, are listed in Table 2 and sFigures 1–4 (available at the end of this article). At low exposure (2 J/cm^2), TU matrix, Filtek Supreme Ultra, and Filtek Bulk Fill had statistically similar DC that failed to surpass 50% ($P > .94$). At this exposure level, SDR Flow+ achieved the highest conversion (SD) (54.45% [0.25%]), though not statistically different from the experimental control and TU filler. At 24 J/cm^2, conversion ranged from 52% through 67% and statistically increased for all groups according to the pairwise *t* test, except for the experimental control ($P = .056$). TU filler and the Filtek Bulk Fill had the greatest statistically significant increases using the *t* test ($P < .005$, as noted by the double asterisks in Table 2) from 50.78% to 66.92% and 45.17% to 59.45%, respectively.

TU-modified composites had lower Rp_{max} than the experimental control ($P < .001$; Figure 1). The Rp vs conversion curves for TU-modified materials presented a quasiplateau region with slower deceleration past Rp_{max}. In addition, these materials had a distinct delay in the onset of deceleration (denoted by * and ** in Figure 1) compared with experimental control and commercial materials, which showed behavior more consistent with methacrylate polymerizations in which the Rp_{max} coincides with the onset of deceleration.[31] The presence of TU on the filler surface vs matrix dispersion did not result in statistical differences in Rp_{max} ($P = .166$), DC at Rp_{max} ($P = .239$), or DC at high exposure ($P = .132$), but at low exposure, the TU matrix reached a lower final conversion than TU filler (45.92% vs 50.78%; $P = .027$). Of all materials tested, SDR Flow+ had the highest Rp_{max} (statistically similar to the experimental control) and DC at Rp_{max} (5.10 ± 0.08% and 18.53 ± 0.08% per second, respectively).

The inset table in Figure 1 lists the conversion at the onset of deceleration for each material. The DC at Rp_{max} value was used to estimate the onset of deceleration for each of the materials, with the exception of TU matrix and TU filler (onsets denoted by * and **, respectively). The conversion at the onset of significant deceleration (DC at RPmax) for both TU materials was more than double the conversion of all other composites, with the exception of SDR Flow+. The lowest conversion at onset was seen in Filtek Bulk Fill, which reached approximately 11%. The points in the curve corresponding to the stage of polymerization at which the light was turned off are marked with Ø in sFigure 5 (available at the end of this article).

Polymerization stress

The final stress values (SD) ranged from 3.3 (0.3) megapascals (Filtek Supreme Ultra) through 0.6 (0.1) megapascals (TU filler) (sFigure 6, available at the end of this article). The incorporation of TU reduced polymerization stress significantly (Figures 2 and 3, Table 3). TU matrix had 55% lower stress than the experimental control, and TU filler had a 78% reduction ($P < .001$). Comparing the commercial composites, the Filtek Bulk Fill and SDR Flow+ had 34% ($P = .001$) and 43% ($P < .001$) lower final stress than the Filtek Supreme Ultra, respectively. Table 3 compares the stress buildup at the end of photoactivation (at 20 seconds) with the final stress (at 600 seconds). The polymerization stress ratio is defined as the stress at 20 seconds divided by the final stress and differed significantly among the groups ($P = .002$). The control composites (experimental control, Filtek Supreme Ultra) had the highest stress ratios, whereas the TU-based materials showed both very low stress at the end of photocuring and the lowest overall final stress values and stress ratios.

Stress relaxation

Figure 4 shows postpolymerization isothermal stress relaxation measured using DMA (125 °C). The curves generally show a rapid drop in modulus, followed by steady-state behavior, which was reached after approximately 10 minutes. The relative change in relaxation modulus was greatest in the TU matrix, TU filler, and SDR Flow+ groups ($P < .0001$), which all relaxed by at least 70% in comparison with the initial modulus (Figure 4 and sFigure 7, available at the end of this article). The maximum reduction was observed in the SDR Flow+ (77%). The experimental control, Filtek Supreme Ultra, and Filtek Bulk Fill displayed the least amount of relaxation, with a maximum relaxation of approximately 56%.

The rates of stress relaxation were investigated by comparing the time required for the composite groups to relax to 50% of the initial modulus at 125 °C (Figure 5A). The relaxation times were statistically similar for SDR Flow+, TU filler, and TU matrix, with average relaxation times of 2.0, 2.7, and 3.7 minutes, respectively. The average relaxation times more than doubled for Filtek Supreme Ultra, Filtek Bulk Fill, and the experimental control (6.5, 8.4, and 8.8 minutes, respectively). The variation in modulus at 125 °C is shown in Figure 5B. Filtek Supreme Ultra showed the highest modulus at this temperature, followed by the experimental control and SDR Flow+. Filtek Bulk Fill, TU matrix, and TU filler displayed the lowest moduli and were not statistically different from each other ($P > .989$).

In addition, the initial elastic modulus (E_0) at 80 °C (sFigure 7, available at the end of this article) showed statistical differences among the groups ($P = .003$), with the commercial materials having the highest results but statistically similar to the TU-containing materials. The experimental control had the lowest E_0 at 80 °C.

Discussion

The RBCs selected for this study highlight unique resin chemistries that have the potential to facilitate stress reduction either during photopolymerization or after the polymer network has been established. Although the commercial materials differed in resin composition and filler weight fractions, some variation in Rp_{max}, conversion at vitrification, and conversion at the onset of deceleration can likely be ascribed to the novel chemistries contained within the resins. The rate vs conversion profiles revealed significant differences in kinetic behavior between both commercial and experimental composites (Figure 1). The Rp_{max} of TU matrix and TU filler systems was reduced by 50% or more compared with the experimental control. This behavior has been reported previously in both resins and composites modified with TU oligomers.[32,33] In conventional methacrylate systems, the Rp_{max} generally coincides with the start of deceleration and signifies the onset of vitrification.[34] In addition, a sharp downturn after Rp_{max} is typical of chain polymerizations.[7] In the TU-modified materials in this study, there was a significant plateau, or induction time, between the occurrence of Rp_{max} and the onset of more significant deceleration. In fact, the conversion at the onset of deceleration for TU matrix and TU filler, at approximately 30%, was more than double that of the experimental control and the commercial materials. This suggests that the onset of significant diffusion limitations for propagation and termination events are delayed to higher conversions in the materials containing TU.[15,34] The effect of the thiol chain transfer from the TU oligomers to the surrounding methacrylate matrix resin is to reduce the average kinetic chain length, allowing for higher conversion to be achieved before the reaction diffusion controlled stage sets in.[35] The lack of statistical difference in DC, Rp_{max}, or DC at Rp_{max} between Filtek Bulk Fill and Filtek Supreme Ultra would suggest that the incorporation of addition-fragmentation monomer did not radically alter the reaction kinetic profile of the composite even though it played a substantial role in polymerization stress reduction, as discussed in more detail later. The SDR Flow+ had the highest DC at Rp_{max} of the commercial materials as well as the highest overall conversion at low radiant exposure, highest Rp_{max}, and steepest deceleration slope. Advertised as a bulk fill flowable product, these results combined may be attributed in part to the lower filler content compared with the other commercial materials in our study.[36] In addition, the high molecular weight of the SDR-patented UDMA monomer may be responsible for the elevated Rp_{max} while at the same time postponing the Rp_{max} to higher conversion. The monomer's photopolymerization modulation capability potentially delays the increase in cross-linking, effectively dissipating energy and delaying the onset of vitrification.[11,37]

At low radiant exposure, the TU-modified RBCs had final DCs at or below the experimental control composite. This was somewhat unexpected because the delayed gelation imparted by TU pendant thiol-to-vinyl chain transfer typically delays diffusion limitations, resulting in higher final conversion.[34,38] However, when the radiant exposure was increased to 24 J/cm^2 to replicate clinical conditions better, the TU filler showed the highest overall final conversion at 66.9%, whereas the TU matrix reached 59.2%. However, the experimental control remained virtually unchanged, at 52.2% conversion. The lower conversion observed in the TU matrix at low irradiance could be explained by a combination of 2 main factors: the substitution of 20 wt% of the resin matrix with high molecular weight (> 5 kDa) TU oligomer, combined with additional hydrogen bonding potential, substantially increases the resin viscosity.[39] Furthermore, it would be expected that an increase in viscosity would increase Rp_{max} (limitations to diffusion at low conversion favor propagation reactions instead of termination reactions, leading to a rate increase) but the rate maximum occurred at lower conversion compared with lower viscosity materials.[28] In spite of the previous argument, the TU materials still displayed a lower rate of polymerization, suggesting the effect of chain transfer reactions in reducing the rate was even more pronounced at lower irradiance conditions. In other words, the combination of chain transfer reactions and lower concentration of generated radicals overcame the effect of high viscosity, which would have been expected to increase the rate.[28,40,41] In the case of the TU filler material, localizing the TU to the filler surface not only reduces the overall weight fraction of TU in the composite (≈ 1 wt% compared with 6 wt% for the TU added directly in the matrix), it also reduces the effect of the TU on the overall viscosity of the system,[38] so at low irradiance, the conversion was statistically similar to experimental control, Filtek Supreme Ultra, and SDR Flow+. The increase in conversion from low to high radiant exposure was only 1% for the experimental control but more than 13% for the TU-containing materials. This is explained by the much higher rates of Rp_{max} and deceleration for the control, which translated to an early reduction in network mobility and caused the limited conversion to be around 52%. For the commercial materials, a similar trend was observed; Filtek Bulk Fill increased by 14%, and SDR Flow+ increased by nearly 10%, whereas Filtek Supreme Ultra increased by less than 8%. Compared with typical high-viscosity, cross-linking dimethacrylates, materials that are capable of undergoing chain transfer, or have other network-adaptable mechanisms, see the onset of vitrification occurring at higher conversions.[31] Shortly after that, propagation becomes diffusion-controlled as the rate declines during deceleration and limiting conversion is reached.[41] Therefore, stress-inducing conversion (ie, the conversion that takes place after vitrification) is minimized. Indeed, here, the experimental control displayed the second highest Rp_{max} and deceleration, only behind that of the lower viscosity, network-adaptable SDR Flow+, which, again, was associated with higher values of stress for the control.

Polymerization stress was significantly reduced in the low-stress commercial RBCs and TU-modified materials compared with Filtek Supreme Ultra and the experimental control. Filtek Bulk Fill had 34% lower stress than the Filtek Supreme Ultra while displaying a similar kinetic profile, in spite of the approximately 2% higher filler weight fraction of the former (Table 1). This is likely because of radical-promoted dynamic exchange reactions, which are complementary to the polymer network formation and facilitate stress reduction without compromising final conversion.[42,43] SDR Flow+ has been well established as a low-stress flowable composite owing to photopolymerization modulation during network formation, delaying gelation and mitigating early buildup of shrinkage stresses.[11,12,44] In this study, this was evident from the high DC at Rp_{max} (18.5 ± 0.1%), the 43% lower final stress compared with Filtek Supreme Ultra, the low rate of stress buildup during the 20-second photoactivation time, and the reduced polymerization stress ratio (0.31 for SDR Flow+ vs 0.55 for Filtek Supreme Ultra). As for the experimental materials, after the light was turned off, the conversion progressed much farther in the dark for the material containing TU filler, eventually reaching a similar conversion to the experimental control, for which the light going off happened much closer to vitrification (the final inflection points on the graph in sFigure 1, available at the end of this article). In other words, for all commercial materials and the experimental control, the radiant exposure at 20 seconds was enough to drive the materials almost to complete vitrification, with a steeper deceleration rate than the TU-containing materials. This is explained by the fact that the non-TU materials had reached close to limiting conversion at 20 seconds, whereas conversely, for the TU-containing materials, the conversion at 20 seconds was lower and therefore, some degree of mobility was still preserved, which ultimately led to the final conversion being similar to the experimental control.

The lowest overall polymerization stress rates and final values were seen in the TU matrix and TU filler groups. This is consistent with prior studies,[45–48] which have shown substantial stress reductions in both dental resins and RBCs modified with TU. The introduction of high molecular weight, low glass transition temperature (Tg), and TU oligomer to some extent limits volumetric shrinkage, another key stress determinant, and the chain transfer mechanisms imparted by pendant thiols on the TU molecule also enable stress reduction by extending the previtrification regime,[34] without sacrificing the final DC.[4,34,39] By localizing the TU at the resin-filler interface, much greater stress reduction was achieved with a similar TU concentration than the TU matrix group, and with the consequent advantage of increased fracture toughness, as previously shown.[15] The added benefit of improved composite handling properties suggests interfacial targeting is a highly effective strategy for stress mitigation.[24,49] The compliance of the stress test apparatus was high, which better correlates with the clinical situation (though not perfectly) compared with fixed strain, low compliance systems using an extensometer.[50] However, 1 limitation of this study is that we can only indirectly correlate stress, conversion, and modulus development. Concomitant measurements of conversion and stress or modulus development could further elucidate differences in polymer network formation within these materials with unique chemistries, some of which result in delayed gel point conversion.[34,51] In our study, the modulus at each temperature can be derived from the stress relaxation curves, discussed in more detail below.

Postpolymerization stress relaxation of RBCs is an important parameter that can affect the longevity of clinical restorative materials and can be differentiated from polymerization stress by using DMA to examine the viscoelastic properties of fully polymerized materials under isostrain or isothermal conditions. At the lowest temperature tested here (80 °C), all the materials had similar E_0 (sFigure 7, available at the end of this article). One potential limitation of our study is that the temperatures used in the stress relaxation study were too high to be clinically relevant. However, the temperatures at which the test was run aimed at accelerating the stress relaxation that would eventually take place in these materials over a longer period at body temperature.[52,53] Moreover, some of the stress relaxation strategies used by the manufacturer are meant to take effect during polymerization, in which mobility is much higher than in the glassy material that results after polymerization; this is another reason why we opted for running these tests near or above the Tg of these materials.[53] The characteristic relaxation time (**τ**) (Figures 4 and 5) can be used to differentiate rates of relaxation among materials as well as to calculate activation energies for thermally-triggered exchange reactions[42,54]; **τ** is traditionally equal to the point at which the material modulus relaxes to 1/e (Euler number e, 2.71828) on the basis of the Maxwell model for viscoelastic stress relaxation.[19,55,56] However, unlike thermosets such as elastomers and unfilled resins, commercial RBCs have much greater stiffness and modulus because of high inorganic filler content. As a result, the material is limited in the amount of relaxation that can occur, and this is further restricted near clinical use temperatures, which are typically well below the Tg of the material. Therefore, for our study, the 50% relaxation threshold was selected as **τ** to compare relaxation times among the materials, whereas 125 °C was chosen to provide sufficient relaxation to differentiate among the RBCs.

The most rapid stress relaxation was observed in SDR Flow+, TU matrix, and TU filler, which is in part explained by their lower filler content.[57] In addition, low Tg TU additives impart greater toughness to the composite, which may have resulted in faster relaxation but also reduced the modulus at this temperature (Figure 5B).[58] A previous study involving TU-modified composites have shown that modulus at clinical use temperatures is not reduced, but fracture toughness is improved.[14] Furthermore, because SDR Flow+, TU matrix, and TU filler showed the highest conversions at the onset of deceleration, it can be speculated that these materials may have been more homogeneous and less cross-linked, thus facilitating more postpolymerization stress relaxation. In the SDR Flow+, lower cross-link density may be attributed to the breaking of the photomodulator monomer during light exposure, assuming some of those bonds do not reform after the light is extinguished. Previous articles have shown that TU-modified composites and cement have similar[14] to lower cross-link density.[33] Furthermore, they have the added potential for stress relaxation enhancement because of dynamic covalent mechanisms such as the reversion of thiocarbamates to thiol and isocyanate moieties and vice versa, which has been shown to occur at temperatures around 120 °C.[18] This can occur in the presence of a base catalyst such as a tertiary amine. In addition, the stoichiometric excess of thiols on the TU molecule could facilitate additional exchange reactions when the tertiary amine ethyl-4-dimethylaminobenzoate is present. The moduli of both Filtek Bulk Fill and SDR Flow+ were significantly lower than Filtek Supreme Ultra at 125 °C, but the Filtek Bulk Fill did not exhibit a faster relaxation time vs Filtek Supreme Ultra. This is in line with the presumption that the AFT monomer is effective at reducing stress during polymerization via radical-mediated exchange mechanisms but does not play a significant role in relaxing stresses in a fully formed and highly cross-linked network.[49]

Finally, it is important to highlight that the aim of our study was not to test the fracture toughness of these materials directly nor the volumetric shrinkage or optical properties, all of which are relevant to the strength of materials. All of these aspects have been covered in previous articles (volumetric shrinkage,[32] optical properties,[25] and matrix-filler interface[24]). It has been shown that, in spite of the high molecular weight, the presence of TU does not affect volumetric shrinkage because it also leads to increased conversion[32] (as already mentioned), light transmission in depth,[25] and fracture toughness.[24] In this study, we focused on evaluating a distinct aspect of this complex equation, which has not been as well-explored in the literature, which was to elucidate the mechanisms that led to the observed increase in fracture toughness observed previously,[16,33,39] some of which cannot be explained by toughening given by the more flexible TU bonds. The main goal here was to conduct an in-depth analysis of the polymer structure, to use well-established stress relaxation techniques in dynamic mechanical analysis, and to explain reduced polymerization stress and fracture toughness with TU-based materials, using commercial materials with claimed stress-relaxation behavior as benchmarks.

Conclusions

This study highlighted 3 unique polymer-chemistry-based approaches toward addressing the problem of polymerization stress generation in dental composites. The stress-reducing strategies used in both commercial materials tested were effective. TU-modified composites showed substantial stress reduction and stress relaxation through thiol chain transfer mechanisms. The materials in this study differed substantially in kinetic behavior, but final conversions and elastic moduli were generally not compromised compared with the control materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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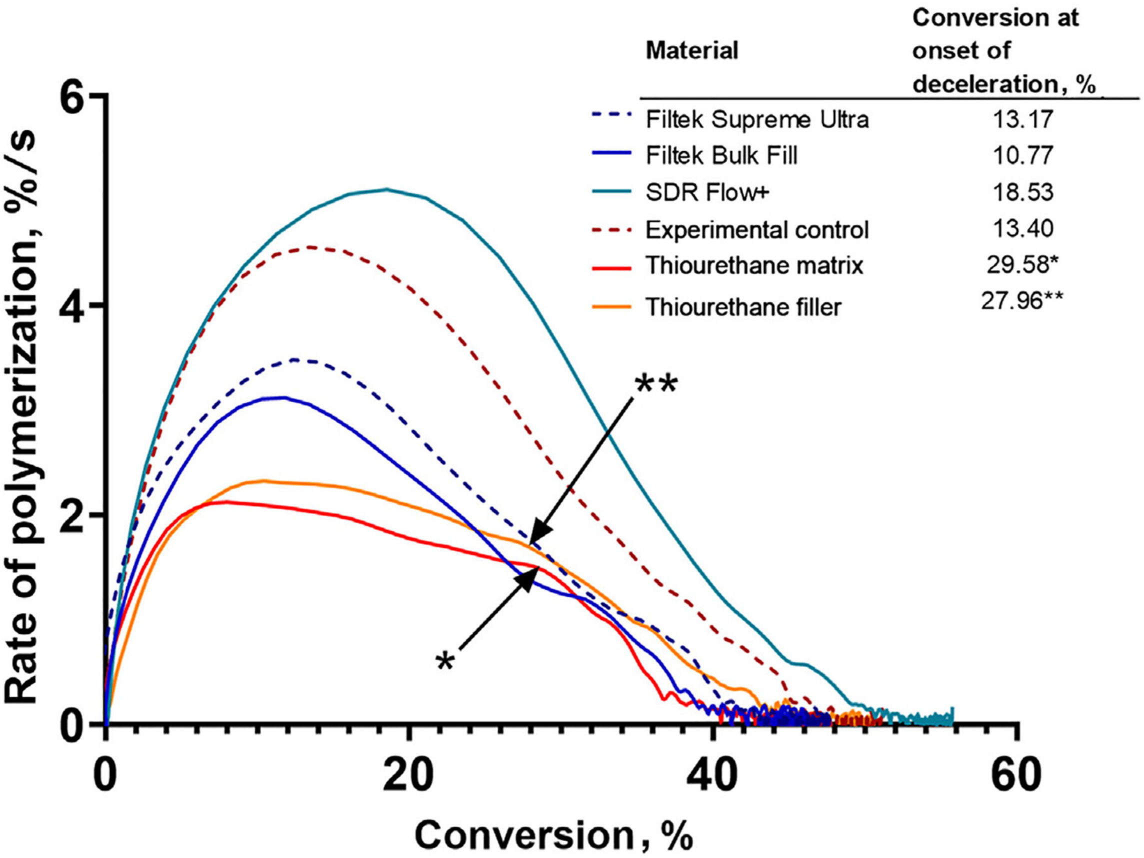
Why Is This Important?

Polymerization stress and related gaps still pose a challenge to restoration longevity. The authors showed that thiourethane-modified experimental composites may be an alternative stress-relieving mechanism to eventually impart reduced gap formation during polymerization and reduced crack propagation in the postpolymerized stage. Ultimately, this has translational potential for improving the lifetime of esthetic restorations.



Material	Conversion at onset of deceleration, %
- - - Filtek Supreme Ultra	13.17
— Filtek Bulk Fill	10.77
— SDR Flow+	18.53
- - - Experimental control	13.40
— Thiourethane matrix	29.58*
— Thiourethane filler	27.96**

Figure 1.

Rate of polymerization vs degree of conversion plotted for all materials (radiant exposure = 2 J/cm^2. Dashed lines denote experimental and commercial controls. Asterisks indicate the onset of deceleration for TU matrix (*) and TU filler (**). The inset table lists the percentage conversion at the onset of deceleration. Filtek Bulk Fill: Filtek Bulk Fill Posterior Restorative (3M ESPE). Filtek Supreme Ultra: Filtek Supreme Ultra Universal Restorative (3M ESPE). SDR Flow+: SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona).

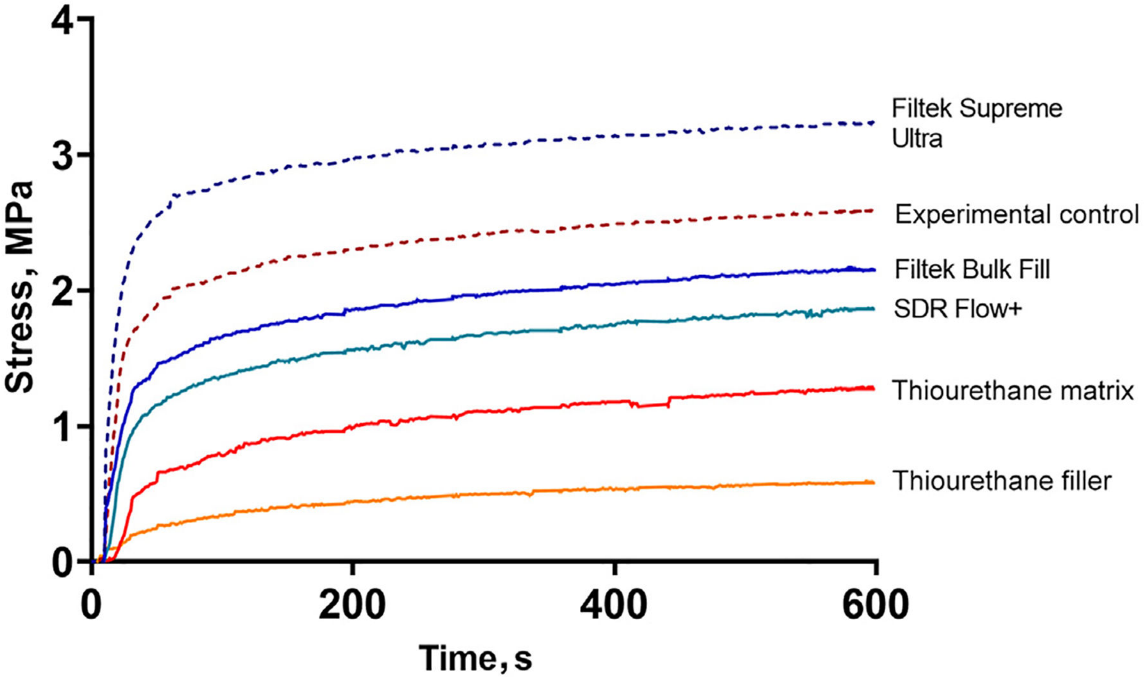


Figure 2.

Polymerization stress vs time plotted for all groups (radiant exposure = 2 J/cm^2). Dashed lines denote experimental and commercial controls. Filtek Bulk Fill: Filtek Bulk Fill Posterior Restorative (3M ESPE). Filtek Supreme Ultra: Filtek Supreme Ultra Universal Restorative (3M ESPE). MPa: Megapascal. SDR Flow+: SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona).

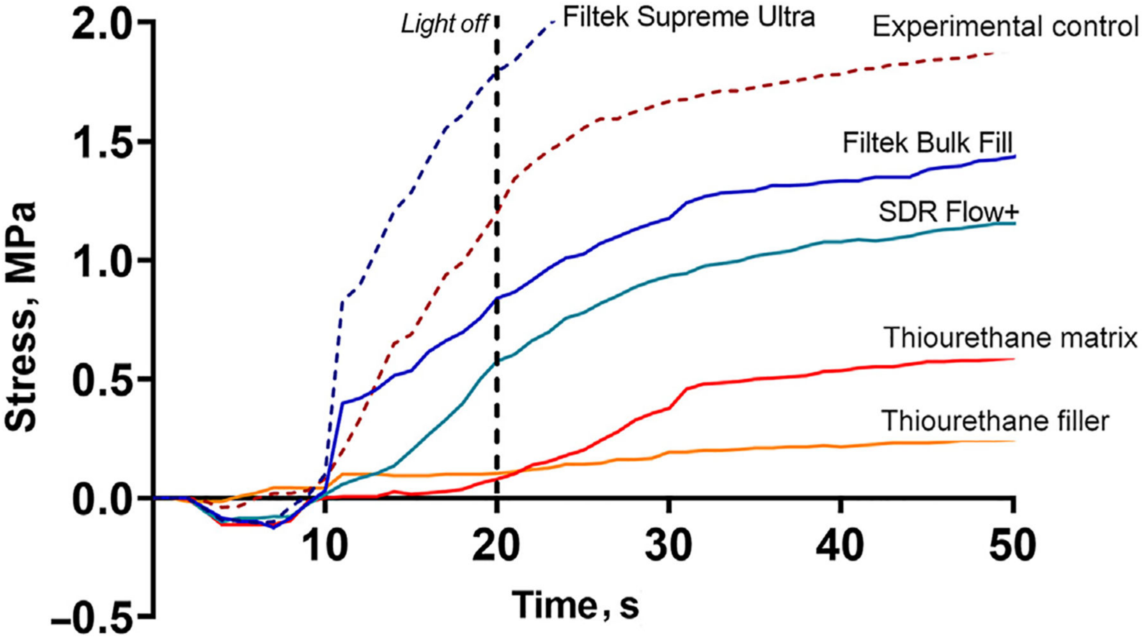


Figure 3.

Polymerization stress vs time plotted for all groups, highlighting early-stage stress development. Dashed lines denote experimental and commercial controls. The vertical dashed line indicates the photocuring end point (radiant exposure = 2 J/cm^2). Filtek Bulk Fill: Filtek Bulk Fill Posterior Restorative (3M ESPE). Filtek Supreme Ultra: Filtek Supreme Ultra Universal Restorative (3M ESPE). MPa: Megapascal. SDR Flow+: SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona).

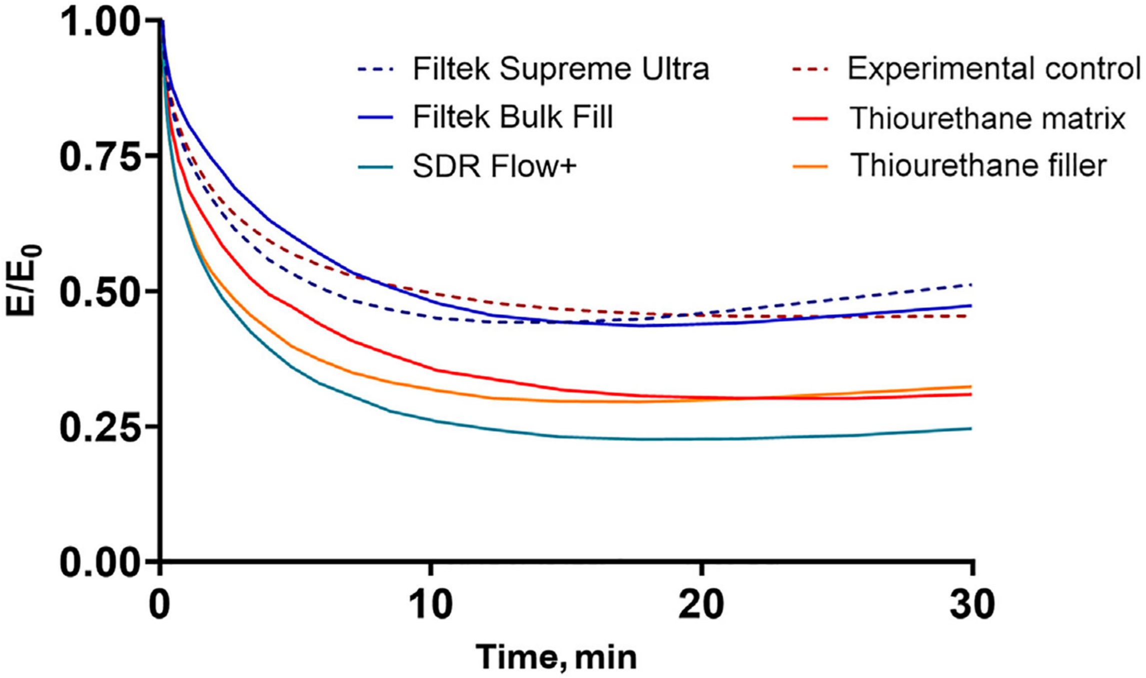


Figure 4.

Viscoelastic stress relaxation was expressed as the ratio of modulus as a function of time, and the initial modulus normalized to 100% (1.0 ratio) for all samples measured using dynamic mechanical analysis (0.05% strain, 30 minutes deformation time, 125 °C). Dashed lines denote experimental and commercial controls. E: Ratio of modulus. E_0: Initial modulus. Filtek Bulk Fill: Filtek Bulk Fill Posterior Restorative (3M ESPE). Filtek Supreme Ultra: Filtek Supreme Ultra Universal Restorative (3M ESPE). SDR Flow+: SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona).

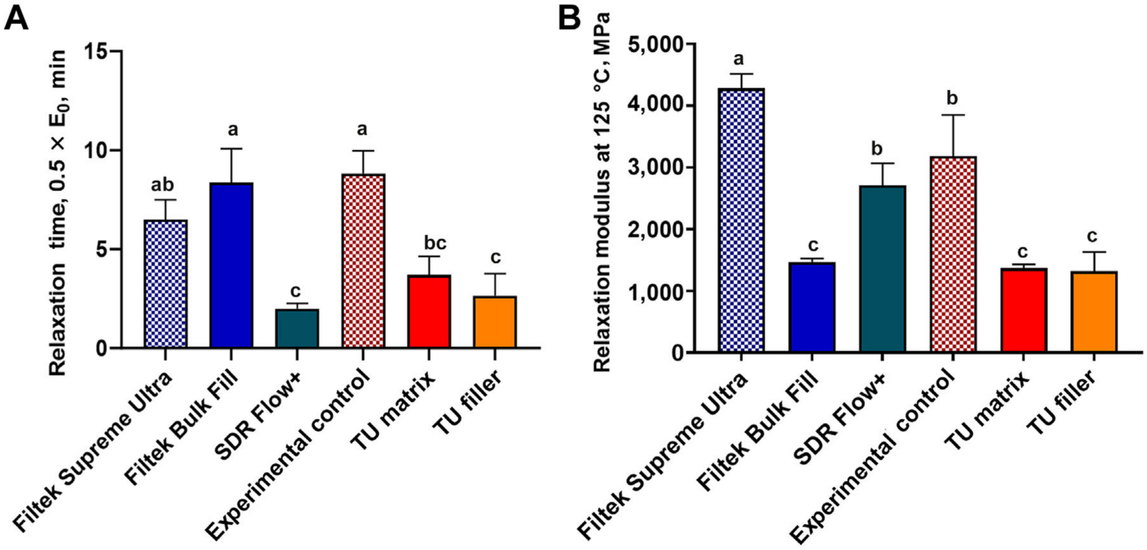


Figure 5.

Characteristic relaxation times (**A**) and relaxation modulus (**B**) for all composite groups at 125 °C. The characteristic relaxation time is defined as the time required for the material to relax to 50% of the initial modulus ($0.5 \times E_0$). Checkered infill denotes experimental and commercial controls. Letters indicate statistical similarity among groups ($P > .05$). E_0: Initial modulus. Filtek Bulk Fill: Filtek Bulk Fill Posterior Restorative (3M ESPE). Filtek Supreme Ultra: Filtek Supreme Ultra Universal Restorative (3M ESPE). SDR Flow+: SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona). TU: Thiourethane.

Table 1

Composition of commercial and experimental resin-based composites.

Material	Manufacturer[*]	Resin Matrix	Filler	Filler, Wt %
Experimental control	Experimental	BisGMA,[†] UDMA,[§] TEGDMA[¶]	0.7 μm barium silicate,[‡] OX 50 fumed silica	70.0
TU[**] matrix	Experimental	BisGMA, UDMA, TEGDMA, TU oligomer	0.7 μm methacrylate-silanized barium silicate, OX 50 fumed silica	70.0
TU filler	Experimental	BisGMA, UDMA, TEGDMA	0.7 μm TU-silanized barium silicate, OX 50 fumed silica	70.0
Filtek Supreme Ultra Universal Restorative	3M ESPE (lot no. N928816)	BisGMA, UDMA, TEGDMA, ethoxylated bisphenol A dimethacrylate, polyethylene glycol dimethacrylate	Nonaggregated 20 nm silica, 4–11 nm zirconia, aggregated zirconia and silica cluster filler	78.5
Filtek Bulk Fill Posterior Restorative	3M ESPE (lot no. N683932)	Proprietary aromatic UDMA, proprietary addition-fragmentation monomer, dodecanediol dimethacrylate, UDMA	Nonaggregated 20 nm silica, 4–11 nm zirconia, aggregated zirconia and silica cluster filler, 100 nm ytterbium fluoride filler	76.5
SureFil SDR Flow+ Posterior Bulk Fill Flowable Base	Dentsply Sirona (lot no. 00017339)	Proprietary UDMA, ethoxylated bisphenol A dimethacrylate, TEGDMA, trimethylolpropane trimethacrylate	Barium-aluminum-fluoride borosilicate, strontium-aluminum-fluoride silica filler, ytterbium fluoride, fumed silica	70.5

[*] Compositions for commercialmaterials are provided by manufacturers.

[†] BisGMA: Bisphenol-A-diglycidyl dimethacrylate.

[‡] The 0.7 μm barium silicate had the surface treated with a methacrylate silane and was used as received from the supplier.

[§] UDMA: Urethane dimethacrylate.

[¶] TEGDMA: Triethylene glycol dimethacrylate.

[**] TU: Thiourethane.

Table 2

Values for the DC[*] at low radiant exposure (180 s, 2 J/cm^2), DC at high radiant exposure (180 s, 24 J/cm^2), Rp_{max},[†] and DC at Rp_{max}.[‡]

Material	DC at 180 s, 2 J/cm^2, mean (SD), %[§]	DC at 180 s, 24 J/cm^2, mean (SD), %[§]	Rp_{max}, mean (SD), %/s[§]	DC at Rp_{max}, mean (SD), %[§]
Experimental control	51.12 (1.17)^{ab}	52.18 (0.40)^{c}	5.01 (0.23)^{a}	13.40 (0.98)^{b}
Thiourethane matrix	45.92 (0.29)^{c}	59.21 (0.14)abc,[¶]	2.14 (0.03)^{d}	9.07 (2.27)^{c}
Thiourethane filler	50.78 (3.45)^{ab}	66.92 (0.79)^{a,}[**]	2.60 (0.40)^{cd}	11.34 (0.84)^{bc}
Filtek Supreme Ultra Universal Restorative (3M ESPE)	46.42 (0.50)^{bc}	54.18 (1.33)bc,[¶]	3.48 (0.14)^{b}	13.17 (0.93)^{b}
Filtek Bulk Fill Posterior Restorative (3M ESPE)	45.17 (0.13)^{c}	59.45 (4.52)^{abc,}[**]	3.12 (0.11)^{bc}	10.77 (0.47)^{bc}
SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona)	54.45 (0.25)^{a}	63.86 (3.78)ab,[¶]	5.10 (0.08)^{a}	18.53 (0.08)^{a}

[*] DC: Degree of conversion.

[†] Rp_{max}: Maximum rate of polymerization.

[‡] Rp_{max} and DC at Rp_{max} values were determined using low radiant exposure (2 J/cm^2).

[§] Column values with the same superscript are statistically similar ($P > .05$).

[¶] Statistical difference between DC values obtained with 2 or 24 J/cm^2 (t test; $P < .05$).

[**] Statistical difference between DC values obtained with 2 or 24 J/cm^2 (t test; $P < .005$).

Table 3

Comparison of polymerization stress at 20 s (photocuring end point), final stress at 600 s, and the ratio of 20 s stress to final stress.

Material	**Stress at 20 s, MPa***	**Final Stress, MPa***	**Polymerization Stress Ratio***
Experimental control	1.27 (0.13)^{b}	2.59 (0.28)^{b}	0.46 (0.08)^{ab}
Thiourethane matrix	0.08 (0.03)^{d}	1.29 (0.13)^{d}	0.06 (0.02)^{e}
Thiourethane filler	0.10 (0.07)^{d}	0.59 (0.06)^{e}	0.18 (0.08)^{d}
Filtek Supreme Ultra Universal Restorative (3M ESPE)	1.80 (0.20)^{a}	3.25 (0.31)^{a}	0.55 (0.12)^{a}
Filtek Bulk Fill Posterior Restorative (3M ESPE)	0.84 (0.30)^{bc}	2.15 (0.01)^{bc}	0.39 (0.13)^{bc}
SureFil SDR Flow+ Posterior Bulk Fill Flowable Base (Dentsply Sirona)	0.58 (0.11)^{c}	1.86 (0.34)^{cd}	0.31 (0.01)^{c}

[*] Column values with the same superscript letter are statistically similar ($P > .05$).