Polymerization Shrinkage, Stress, and Degree of Conversion in Silorane- and Dimethacrylate-Based Dental Composites

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ABSTRACT: To compare two kind of resin-based dental composites, the polymerization shrinkage, contraction stress (CS), and degree of conversion (DC) of four dimethacrylate-based and one silorane-based composite were investigated. To determine shrinkage, the composites were packed, respectively, into a cylindrical cavity in human teeth and imaged using X-ray microcomputed tomography to determine the precise volume before and 30 min after photopolymerization. To determine CS, the sample was applied in a similarly sized cylinder in a universal testing machine and monitored for 30 min. FTIR spectroscopy was used to determine DC. The volumetric shrinkage (range: 1.1–3.1%) and maximum CS (range: 1.2–3.5 MPa) differed significantly among the tested composites but not the final DC (range: 62.3–69.1%). The silorane-based composite displayed the lowest volumetric shrinkage and CS of all composites. No correlation was observed between the stress and volumetric shrinkage values of the dimethacrylate-based composites. A moderate correlation was found between stress and DC ($r = 0.836$), which was significant at 20 and 40 s. The silorane-based composite exhibited superior shrinkage behavior compared with conventional dimethacrylate composites with comparable polymerization kinetics. The CS was dependent on multiple variables, including the volumetric shrinkage, DC, and curing rate. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1882–1888, 2011

Key words: polymerization shrinkage; dental polymer; composite; degree of polymerization; FTIR

INTRODUCTION

Polymeric dental composites are widely used as restorative materials because of their superior esthetic and mechanical properties. However, their long-term performance remains unsatisfactory because of the intrinsic problem of polymerization shrinkage. The polymer crosslinking process involves double-bond conversion and covalent bond formation, which are inevitably associated with volumetric shrinkage. This shrinkage causes contraction stress (CS), which in turn can cause microleakage, postoperative sensitivity, marginal discoloration, secondary caries, and/or eventual restorative failure. Substantial effort has been directed toward understanding the mechanisms of composite shrinkage and the subsequent stress,[1–3] and many techniques have been proposed for evaluating composite properties. Dilatometer, linometer, and "bonded-disk" methods have been used to measure the linear displacement in shrinkage,[4,5] while micro-computed tomography (µCT) has been used to visually determine the precise location and volume of a resin composite.[6,7]

The volumetric shrinkage of conventional dimethacrylate monomers used in dental composites (e.g., Bis-GMA and TEGDMA) is reduced in resin composites because of the presence of fillers.[8] Several low-shrink/-stress resin alternatives have also been proposed. Silorane resins are derivatives of siloxane and oxirane monomers composed of a hydrophobic siloxane backbone with oxirane rings.[9] These monomers polymerize with a cationic ring opening and provide reduced shrinkage ($\sim$ 1 vol %).[10] However, the low shrinkage rate of resin composite does not seem to reduce the CS. Indeed, the low-shrinkage hybrid composites Aelite LS and Inten-S exhibit CS values that are similar to or higher than those of conventional hybrid composites.[11]

The CS of resin composites is affected by extrinsic (i.e., cavity configuration, photoactivation method, and substrate compliance[12–14]) and intrinsic factors [i.e., degree of conversion (DC), volumetric shrinkage, polymerization rate, and viscoelasticity[2,15]], which interact and influence the stress development process to various degrees. Composites based on the same resin system and polymerization mechanism may actually display similar volumetric shrinkage but different stress values because of differences in

TABLE I
The Composition, Type, and Manufacturer of Resin Composites Used in This Study

Materials	Composition	Composite type	Manufacturer
TPH Spectrum	77-wt % BaAl borosilicate glass filler (<1.0 μm), silicon dioxide (0.04 um), Bis-GMA adduct/Bis-EMA/TEGDMA	Microhybrid	Dentsply, Caulk Milford, DE, US
Venus	Bis-GMA,TEGDMA, 78-wt % X-ray opaque filler, BaAlBF silica glass (0.7 μm), silicon dioxide (0.01–0.04 μm), PI	Microhybrid	Heraeus Kulzer, Hanau, Germany
Valux	Bis-GMA, TEGDMA, 85-wt % zirconia/silica (0.01–3.5 μm)	Microhybrid	3M ESPE, St. Paul, MN, US
Clearfil Majesty	Bis-GMA, TEGDMA, ArDMA, 92-wt % filler, alumina, glass-ceramic (<40 μm)	Nanohybrid	Kuraray, Okayama, Japan
Filtek P90	Silorane (3,4-epoxycyclohexylethylcyclo polymethylsiloxane, bis-3-4-epoxycyclohexyl ethyl-phenylmethysilane), 76-wt % filler, silicon dioxide, ytterbium trifluoride	Microhybrid	3M ESPE, St. Paul, MN, US

the elastic modulus or reaction rate. The mechanisms involved in composite stress development are quite complex and differ greatly between silorane and dimethacrylate resin systems. In silorane systems, an oxaspirocyclic core enables the double ring-opening polymerization required for volume expansion via cationic intermediates, which reduces the polymerization shrinkage. Bulk shrinkage in dimethacrylate systems arises from covalent bond formation via the vinyl functional group and radical intermediates. This process unites the monomer units and reduces their mobility as part of an extended polymeric structure. It is unclear whether the polymerization behavior of these two distinct resin systems is correlatable. For this reason, it is of interest to investigate polymerization behavior and interactions of factors in the two resin systems respectively. For the dimethacrylate system, four hybrid composites were selected in considering of universal application and uniform composition.

The aims of this study are: (1) to compare the polymeric behavior of a silorane-based composite with four conventional dimethacrylate-based composites and (2) to evaluate the correlation between the shrinkage stress and other polymer properties. The tested hypothesis is that significant differences existed among the tested materials in terms of their polymeric parameters, which influenced the stress development.

EXPERIMENTAL

Materials

Four conventional hybrid dimethacrylate composites, Valux (VA), Clearfil Majesty (CM), TPH Spectrum (TPH), and Venus (VE), and one silorane-based composite, Filtek P90 (FI), were used in this study (Table I).

Polymerization volumetric shrinkage

Twenty-five sound third human molars were selected and stored in 1% chloramines solution (Solarbio Bioscience and Technology Co., Shanghai, China) at 4°C within 1 month after extraction. The occlusal enamel was cut away with a water-cooled low-speed diamond saw (SYJ-150A, Kejing Co., China). After polishing the dentin surface with SiC abrasive paper (grits from 100 to 600), cylindrical cavities (d: 4 mm and h: 2 mm) were drilled to simulate clinical cavities.

A μCT scanner (SIEMENS Inveon, Germany) was used to image the composites and evaluate their volumetric shrinkage (15-μm line resolution, 800-ms exposure time, X-ray source of 80 kVp, and 500 μA). Uncured resin composite was packed into the cavities, fixed on the CT sample holder, and 1 mm on the top of the samples was cured for 40 s (QHL75, Dentsply, Germany). Cured samples were again scanned by μCT at 30 min after curing. The 2D composite images obtained by μCT were imported into imaging software (ImageJ). 3D images were reconstructed, and the volumes before and after polymerization were calculated.

Degree of conversion

ATR-FTIR spectroscopy (EQUNIOX 55, HELIOS, Germany) was used to measure the double-bond conversions of composite specimens ($n = 5$) before and after the start of irradiation (at 20, 40, and 80 s and 5, 10, and 30 min). Spectra conditions were as follows: 4000–600 cm^{-1} wave range, 4 cm^{-1} resolution, 64 scans coaddition, and 2-μm analysis depth at 1000 cm^{-1}.

The DC was measured with the 2-frequency technique in absorbance mode. For dimethacrylate composites, stretching vibrations of the aliphatic C=C bonds (1636 cm^{-1}) and of the aromatic C—C bonds (1605 cm^{-1}) were used as the analytical and internal reference absorption bands, respectively. For FI, stretching vibrations of the epoxy rings C—O—C (884 cm^{-1}) and of the Si—CH$_3$ bonds (695 cm^{-1}) were used as the analytical and internal reference

TABLE II
Volumetric Shrinkage of Composites 30 min After Curing

Composite	Mean vol % (SD)
CM	2.17[a] (0.12)
VA	2.66[b] (0.16)
VE	3.12[c] (0.09)
TPH	2.72[b] (0.21)
FI	1.10[d] (0.07)

[a,b,c,d] Indicates statistical differences among experimental groups.

absorption bands, respectively. The DC was calculated from the ratio of the peak heights of the analytical and reference absorption bands normalized by the ratio of the unset material:

$$\text{DC} = 1 - \frac{[\text{Abs}_{ana}/\text{Abs}_{ref}]_{cured}}{[\text{Abs}_{ana}/\text{Abs}_{ref}]_{uncured}} \times 100\% \quad (1)$$

In Eq. (1), Abs_{ana} and Abs_{ref} represent the peak heights of the aliphatic C=C bond and the benzene ring (dimethacrylate) or the peak heights of the oxirane C—O—C and Si—CH$_3$ (silorane), respectively.

Contraction stress

Shrinkage-stress kinetics was measured using a universal testing machine (EZ-TEST, SHIMADZU, Japan) in a closed-loop control system. A custom-made stainless-steel rod with a flat polished end was fixed rigidly to the load-cell of the universal testing machine, opposing a glass plate mounted to the stationary part of the machine framework. The flat end of the rod and bonding area of the glass plate were sandblasted to facilitate micromechanical attachment of the resin sample. Resin samples were inserted into a circular holder (*d*: 4 mm) on the glass plate. The crosshead was lowered to set the specimen in a 2-mm height. The amount of unset resin composite per specimen was equivalent for a uniform dimension (*h*: 2 mm and *d*: 4 mm), corresponding to a *C*-factor of 1. The resin sample was light-cured underneath the glass plate for 40 s (QHL75, Dentsply, Germany). The monitor to CS was started from photoinitiation and recorded at intervals in two parts: curing intervals (20 s and 40 s) and postcuring intervals (80 s, 5 min, 10 min, and 30 min).

The axial force (*F*) of resin composites ($n = 5$) with a cross-sectional area *A* of 12.56 mm^2 was expressed as the average stress (F/A) in MPa. Stress rates were calculated as the change in stress as a function of time at each interval during the test period. The maximum stress and stress rate in the test period were also recorded.

Statistical analyses

One-way analysis of variance (ANOVA) and LSD post hoc tests were used to determine differences in the volumetric shrinkage, CS, and DC among the materials, as well as the stress and DC rates between intervals in each composite. Correlations between CS and related properties were evaluated by Pearson's correlation test. An $a = 0.05$ was selected as the significance level for all comparisons. For each parameter, five samples of each of the five composite systems were measured and averaged.

RESULTS AND DISCUSSION

Volumetric shrinkage

Mean volumetric shrinkage values for the tested resin composites ranged 1.1–3.1% (Table II). Consistent with previous studies, the silorane-based composite FI showed the least shrinkage ($P < 0.05$). Significant differences were observed among the dimethacrylate resin composites, with CM and VE showing the lowest (2.2% at 30 min) and highest (3.1%) shrinkage values, respectively, ($P < 0.05$). Post hoc test exhibited no statistical difference between VA and TPH ($P = 0.486$).

Contraction stress and stress rate

Figure 1 displays representative CS versus time curves and stress kinetics profiles for each material. All dimethacrylate composites displayed a sharp increase in CS at 400–600 s from the start of photoinitiation, which continued at a much slower rate after 600 s and subsequently leveled off. No correlation was observed between the CS and volumetric
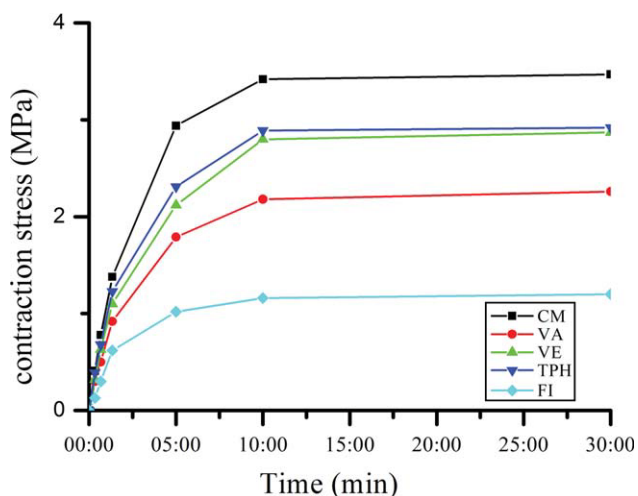

Figure 1 Contraction stress development in composites during and after polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
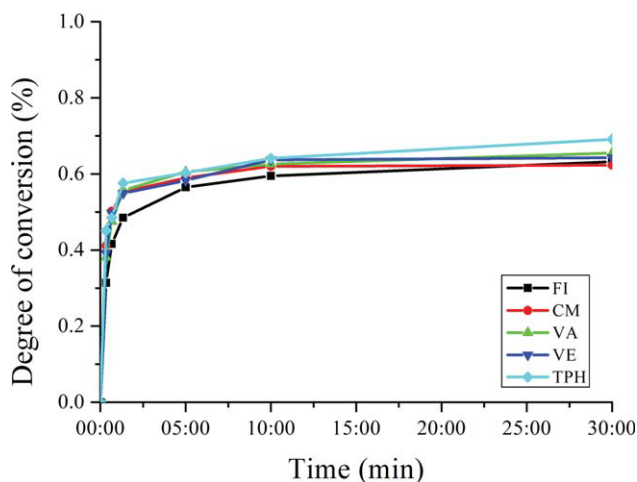
Figure 2 Degree of conversion in composites during and after polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shrinkage for dimethacrylate composites. The silorane composite developed similarly to the dimethacrylate composites, except that it displayed a shorter fast-rising stage (300 s) and a lower maximum stress (1.20 MPa) that correlated with the volumetric shrinkage. The CM stress value (3.47 MPa) was significantly higher than those of VA (2.26 MPa), TPH (2.92 MPa), and VE (2.87 MPa). For all five composite systems, the maximum stress rates (0.015–0.02 MPa/s) were similar and were obtained within the first 20 s.

Degree of conversion and reaction rate

The DC was measured at intervals from the start of photoinitiation (Fig. 2). The DC increased dramatically during the 40-s curing period and continued to rise at gradually declining rates in the postcuring period. Maximum DC values ranged from 62.3% (TPH) to 69.1% (VE). No statistical difference was found in the final DC among tested composites, although the DC of FI was significantly lower than that of the others at 20 and 40 s.

The reaction rate was determined as the change in DC between intervals as a function of time. The reaction rate significantly increased for all resin composites before (but not after) 5 min. An intense increase in DC was observed in the first 20 s of the curing period, especially for CM (41.1%, corresponding to a 0.41-MPa stress increase). Thus, the DC process tended to correlate with stress development.

Polymerization shrinkage is caused by the closer packing of molecules in a polymer network compared with individual monomers and multiple related factors contribute to shrinkage-associated stress development.[2,16,17] The monomer system largely determines the polymerization mechanism and basic properties of a composite. For silorane-based resins, expansion of the cationic ring opening of the cycloaliphatic oxirane

moieties balances the shortening of intermolecular distances, which reduces polymerization shrinkage. In this study, FI displayed reduced volumetric shrinkage and CS values than the conventional dimethacrylate composites, despite the similar elastic moduli, filler contents, and polymeric behavior of the two systems.[18,19] All composites showed a high stress development rate during the early polymerization stage, acquiring >80% of the maximum stress within minutes before gradually leveling off. However, the intense stress build-up for FI was accomplished within 300 s, significantly faster than the corresponding stage for dimethacrylate composites (400–600 s). Given the comparable progress of the reaction, this difference is probably attributable to the low stress of silorane (1.20 MPa) compared with the dimethacrylate composites.

No differences were found among composites in their final DC values, except that FI exhibited a significantly lower DC value than the other composites at 20 and 40 s, which was probably explained by photoinitiation systems. Compared with the double-bond conversion and crosslinking process, more time is needed to form sufficient cations to initiate silorane polymerization.[10] The reaction rate for FI was highest within the first 20 s and decreased thereafter, similar to dimethacrylate composites. A 31.4% increase in DC at a rate of 1.5% s^{-1} corresponded to a 0.13-MPa increase in stress at a rate of 0.0065 MPa/s, which meant 50% of the final DC as well as 10% of the maximum stress value were acquired within the first 20-s curing. It revealed that conversion occurred almost immediately after polymerization was triggered, and despite conversion dependent, the most stress developed after the silorane has reached a significant level of rigidity.

Despite their similar compositions and polymerization processes, significant differences were observed among the dimethacrylate composites, and their CS values were not correlated with the shrinkage levels. VE displayed the greatest volumetric shrinkage but only a median CS, whereas CM exhibited the lowest volumetric shrinkage but the highest CS. These results indicated volumetric shrinkage should not be the only parameter with regard to stress development, and composition may play a role to an extent. It was previously reported that the volumetric shrinkage and filler load are strongly correlated.[19] With the highest filler load (92 wt %) among our tested composites, CM displayed compromised volumetric shrinkage but high CS, probably because the addition of filler presented high viscoelastic behavior,[20,21] characterized by low flow ability at early stages and high elastic modulus (>20 GPa according to manufacturer) later on, which cannot efficiently absorb and compensate shrinkage stresses during polymerization, and resulted in increased stress.

The relationship between filler content and stress is controversial. Several studies have demonstrated that stress is well-correlated with filler content, regardless of differences in matrix composition,[11,22,23] suggesting that viscoelastic properties are more influential on stress development than volumetric shrinkage, while Gonçalves et al.[17] showed that stress is more closely related to shrinkage than to the elastic modulus. However, Kleverlaan and Feilzer[19] have suggested that CS and shrinkage are inversed related. According to Hooke's law, the increment in stress over a certain time interval is proportional to the increase in volumetric shrinkage based on the elastic modulus.[1] High stresses were produced with either no filler (higher shrinkage but lower modulus) or with high filler contents (lower shrikage but higher modulus); minimal stress was observed at intermediate filler loading levels.[3] In this study, neither the volumetric shrinkage nor the elastic modulus dominated stress development. The VA composite, with its median filler load and volumetric shrinkage, exhibited the lowest stress value. A compromise between volumetric shrinkage and viscoelastic behavior could be made to achieve minimal stress. While it has been suggested that the stress of polymer is correlated with filler content,[23] this was not observed here, perhaps due to the discrepant monomer and relatively narrow range of filler contents.

The idea that viscoelastic behavior accommodated much of the volumetric shrinkage was supported by our finding of a moderate correlation between CS and DC ($r = 0.836$). The stress developed in a comparable tendency with DC and a high rate of stress development (400–600 s) corresponded to be 40-s period of rapidly increasing DC. A lag in them suggested that the molecular level chemical reactions led to conversion and then network structure rearrangement. One hypothesis is that the early reaction chain growth was accompanied by plastic deformation, with stress developing in a nearly linear fashion with conversion. As the vitrification stage was approached, the increase in the modulus exceeded the conversion rate. The shrinkage stress continued to rise, even with the slight increase in conversion, because of the reduced capacity for stress-relieving viscous flow and molecular mobility in the highly crosslinked polymer.[4] Thus, most of the stress developed in postcuring stage, although it commenced at very low conversion. Dauvillier et al. also observed a delay between the detectable shrinkage strain and CS, with <10% of the maximum stress being accompanied by 50% of the final value of the shrinkage strain.[24,25] It is reasonable that these two processes occur on different time scales.

The CS is strongly associated with polymerization kinetics,[2,16] with lower reaction rates leading to reduced shrinkage and stress development. A reduc-tion in the curing rate (and therefore the stress rate) may decrease the final stress while maintaining an equivalent DC[26] and also causes better marginal adaptation of a dental composite.[27] In this study, FI produces much lower stress, with an elastic modulus and filler content similar to conventional composites. Besides the lower volumetric shrinkage, the slower curing rates of oxirane materials may also contribute to their lower stress.[18,28] The dimethacrylate composite results confirmed the view that lower CS values are associated with relatively lower reaction rates, especially within the first 20 s. Although VA had a high volumetric shrinkage, it actually exhibited the lowest CS value, partly because of its lower reaction rate within the first 20 s. A moderate correlation was observed between stress and the final DC, and statistical analyses revealed that this correlation was only significant at 20 and 40 s. The reaction rate may be considered as the instant conversion, which was thus more influential on stress than the final conversion. Although the actual instant conversion could not be followed from our spectrometry analysis and no significant differences were observed in the reaction rates, the average value at intervals was general indicator of the conversion level.

As the reaction continues beyond the gel point (at $\sim$ 5% conversion),[4] the maximum reaction rate is generally encountered at $\sim$ 10–20% conversion (depending on the resin viscosity).[29,30] Afterward, the conversion proceeds at a reduced rate. Theoretically, a reduced polymerization rate should delay gelation (or elastic modulus development). More time would be available for viscous flow and chain relaxation, postponing the onset of stress and reducing its magnitude. In contrast, the fast reaction rate of composites does not allow enough time for viscous flow, and it becomes "rigid" within seconds at a relatively low DC.

Microscopic porosity before polymerization reduces the composite shrinkage and stress by generating enlarged voids in the polymer.[31,32] In this study, pores were detected in all tested composites by μCT (Fig. 3), and the internal pores were expanded after curing by contrasting the images before and after in Image J. Alster et al. showed that pores in unfilled resin reduced stress by 17–42%, mainly by increasing the free surface and facilitating flow.[31] Oxygen in the pores may also reduce the DC and stress. The relationship between pores and CS should be further investigated.

Composites in different categories are thought to develop stress similarly[23,33]; however, we observed that the polymeric behavior varied even within the same category. The factors underlying stress development have been a focus of controversy for decades. While some studies implicate conversion
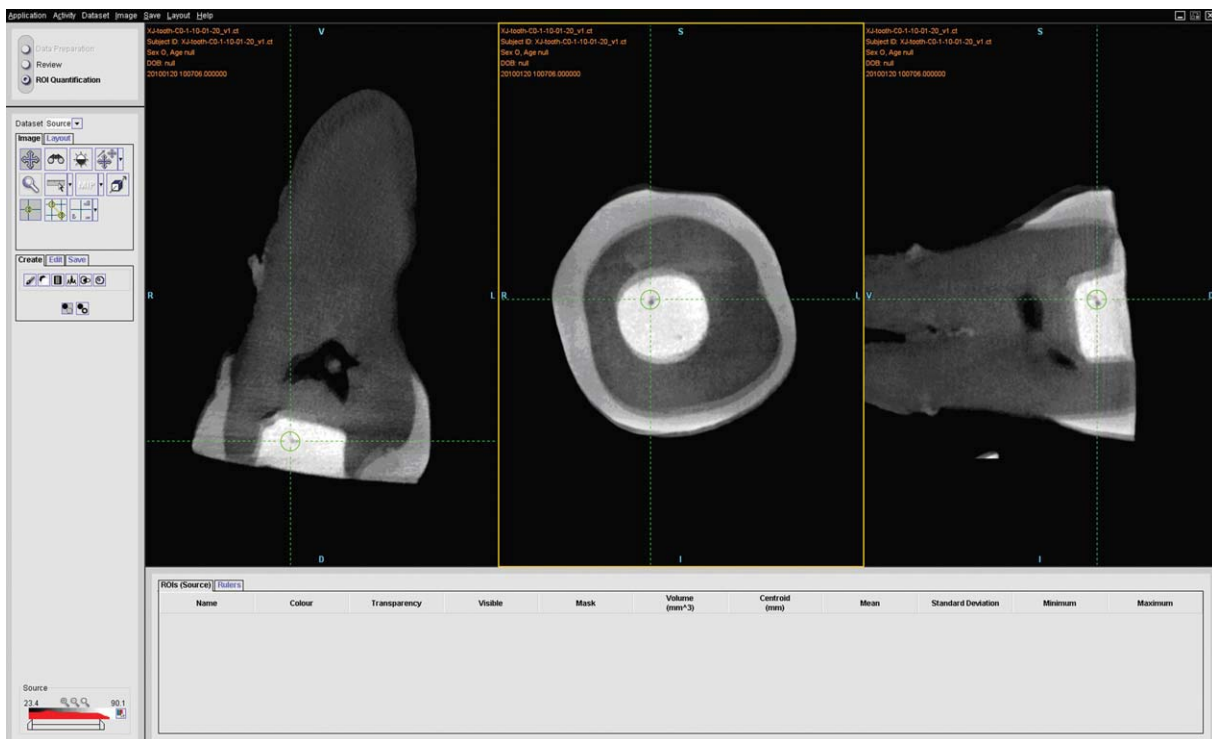
Figure 3 Micro-CT image of internal pores of composite in tooth cavities in three profiles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and its resultant volumetric shrinkage as the most important factors in stress,[27] others have focused on viscoelastic characteristics.[22] A more comprehensive view is that, in a complex, nonlinear fashion, stress development is a product multiple extrinsic factors in addition to the strain and elastic modulus that arise from instant conversion. Any correlation or determining factor identified in previous studies was accompanied by limited conditions. In this study, composites were placed in teeth without adhesive systems to evaluate the free shrinkage pattern of the resin composites, since the intrinsic strain became the only factor affecting dimensional changes. Within the limitations of this *in vitro* study, it is reasonable to assume that composite shrinkage imposed by other external factors in a clinic would vary accordingly. The silorane system demonstrated a promising polymeric behavior and may open new fields in the quest to reduce polymerization shrinkage and balance stress. Exploration of the commercial analog and comparisons among composites would expand our knowledge of the polymerization kinetics of low-shrinkage composites.

CONCLUSIONS

Polymerization shrinkage of tested composites varied both between and among composite types in the two resin systems, but the kinetics patterns were generally comparable. The silorane-based composite exhibited superior polymeric behavior and thus may be a promising alternative to conventional composites. Polymerization-induced stress was a complex function of many factors, including volumetric shrinkage, reaction rate, and elastic modulus. A moderate correlation was found between DC and CS. However, the results cannot be directly translated into the clinical situation without considering the circumstances of application.

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