

# ALTERNATIVES IN POLYMERIZATION CONTRACTION STRESS MANAGEMENT

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**P**olymerization contraction stress of dental composites is often associated with marginal and interfacial failure of bonded restorations. The magnitude of the stress depends on the composite's composition (filler content and matrix composition) and its ability to flow before gelation, which is related to the cavity configuration and curing characteristics of the composite. This article reviews the variations found among studies regarding the contraction stress testing method, contraction stress values of current composites, and discusses the validity of contraction stress studies in relation to results from microleakage tests. The effect of lower curing rates and alternative curing routines on contraction stress values is also discussed, as well as the use of low elastic modulus liners. Moreover, studies with experimental Bis-GMA-based composites and recent developments in low-shrinkage monomers are described.

**UNITERMS:** Composites; Polymerization stress; Elastic modulus; Shrinkage.

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## INTRODUCTION

Dimethacrylate-based composites have been used in dentistry for over 30 years. Developments in filler technology and initiation systems have considerably improved their physical properties and expanded their clinical applications. Notwithstanding, since their early days, the volumetric shrinkage resulting from the conversion of dimethacrylate monomers into long, cross-linked polymeric chains has been identified as a critical limitation that needed to be addressed<sup>11</sup>. Bonding the composite to the cavity walls seemed to be a reasonable solution for the problem. This quest prompted prolific research activity on the subject of dental adhesives and dentin permeability, that brought remarkable advances such as wet bonding and self-etching primers. Unfortunately, in spite of the significant increase in bond strength values reported over the years, the occurrence of microleakage and gap formation, mostly at the dentin/composite interface, did not seem to decrease at a similar rate<sup>49,52</sup>. Concurrently, research on polymerization kinetics and polymerization contraction stress began to intensify, producing enhanced knowledge of the factors influencing the magnitude of forces developed at bonded interfaces.

Dental composite shrinkage ranges between 2 and 6% by volume<sup>61</sup>. Besides volume reduction, chain

growth and cross-linking also result in increased elastic modulus<sup>13,33</sup>. During polymerization, there is a moment, referred to as the *gel point*, when the composite's elastic limit reaches a certain level where its increasing stiffness does not allow enough plastic deformation (or flow) in order to compensate for the reduction in volume. If the composite is bonded to cavity walls, shrinkage forces will start to build-up, resulting in stresses on the bond between the composite and the tooth structure. These forces are not uniformly distributed along the cavity walls<sup>59</sup>. The bond strength between tooth and composite also varies along the bonded surface<sup>83</sup>. Therefore, in areas where the shrinkage forces are higher than the bond strength of the composite to the dental substrate, a gap will develop, increasing the chance for post-operative sensitivity and recurrent caries<sup>18,35</sup>. A recent study demonstrated that the percentage of dentinal gaps in a composite restoration placed "in vivo" may vary between 14% and 54% of the total interface, depending on the materials and techniques employed<sup>45</sup>. Other consequences of the contraction stress reported in the literature are the development of enamel cracks<sup>55,56</sup> and cuspal movement<sup>1,82,88</sup>.

The phenomenon of force development in contracting materials was first described in the dental literature by Bowen<sup>12</sup>. In that study, the author

discussed the influence of the confinement of the setting material as the main factor associated with contraction stress. But it was not until studies by Davidson, et al.<sup>34</sup> and Feilzer, et al.<sup>37</sup> that the subject of polymerization contraction stress began to be studied in depth. It is well established that the magnitude of contraction stress development depends on factors related to the geometry of the cavity preparation (or the testing specimen), as well as on compositional and curing characteristics of the composite.

The most frequent method of measuring contraction stress is the tensiometer<sup>12</sup>. In this test, contraction stress values vary according to the ratio of the bonded to the free surface area of the composite. This ratio has been called the configuration factor, or C-factor<sup>37</sup>. A large unbonded area would facilitate the plastic deformation of the composite during the early stages (or the *pre-gel* phase) of polymerization, reducing the final stress values<sup>39</sup>. This concept has been validated, to a certain extent, by bond strength studies reporting that the microtensile bond strength to deep dentin was lower when the specimens were obtained from restored cavities, compared to specimens obtained from flat dental substrates<sup>72,99</sup>. It was hypothesized that lower bond strengths were caused by a higher incidence of gaps at the dentin interface of the cavity due to higher contraction stresses<sup>99</sup>. Recently, one study verified that the volume of the shrinking composite also influences the stress values<sup>69</sup>. This supports the findings of a previous study that showed that the incidence of marginal gaps in composite restorations was related to the volume of composite and to the bonded area of the cavity walls<sup>46</sup>.

Contraction stress is also determined by characteristics of the composite. Filler content and resin matrix composition dictate the amount of volumetric shrinkage and elastic modulus values of the material<sup>61</sup>. Activation mode, type and concentration of initiators regulate reaction kinetics and degree of conversion<sup>93</sup>. The higher the rate of monomer conversion, the faster the gel point is reached, and the lower is the flow capacity of the material<sup>40</sup>. The higher the degree of conversion, the higher is the composite's final shrinkage and its elastic modulus, both of which contribute to producing higher stresses<sup>14</sup>.

Based on the knowledge accumulated over the years, different approaches have been proposed to reduce the magnitude and the effects of the contraction stress in dental composites. These methods include the incremental placement technique<sup>67</sup>, the development of light units with gradually increasing irradiance or pulsed emission<sup>56</sup>, and the use of low-modulus intermediate layers<sup>92</sup>. Also, modifications of

the current Bis-GMA resin-based composites have been proposed as a means to reduce the stress values without compromising the mechanical properties of the composites<sup>27,29</sup>. The purpose of this article is to discuss the available alternatives to reduce polymerization contraction stress and improve interfacial integrity of direct and indirect bonded restorations based on the scientific evidence.

## CONTRACTION STRESS MEASUREMENTS

Polymerization contraction stress has been evaluated by many different methods. Stress distribution in simulated cavities has been estimated by finite element analysis<sup>6,94</sup> and photoelastic analysis<sup>59,60</sup>. Direct measurements of stress (or strain) are usually accomplished using strain gauges<sup>81</sup> or a tensiometer<sup>12,37,27</sup>. In the typical test set-up with a tensiometer (Figure 1), the composite is placed between two opposing mounting rods (made of metal or glass), one of which is attached to a load cell and the other is attached to a movable cross-head on the testing machine. A feedback system, composed of an extensometer attached to the rods, is used to maintain a constant distance between the rods and to simulate a situation of confinement for the shrinking composite. In this set-up, the value recorded represents the force necessary to counteract the axial shrinkage of the composite and maintain the distance of the rods at its initial value. The nominal stress is calculated by dividing the measured force by the cross-sectional area of the mounting rod.

As in any mechanical test, there is some controversy about a few aspects of the tensiometer method. The main point of dispute seems to be the compliance of the testing system. During the test, some of the contraction force is dissipated through deformation of the components of the testing system (*e.g.*, load cell, mounting rods, adhesive layer). When

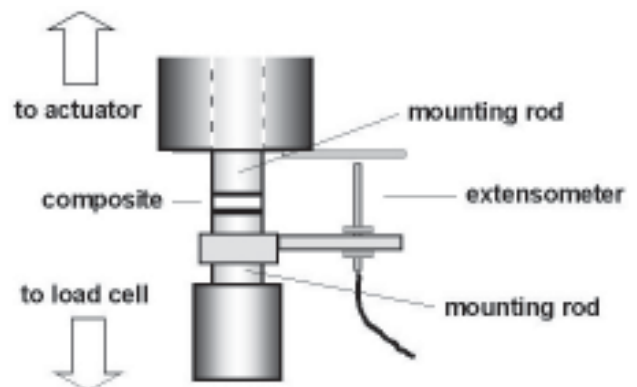


FIGURE 1- Diagram of the contraction stress test set-up

a feedback system is used, the compliance is reduced to a near-zero condition, since virtually all the deformation occurring outside of the extensometer limits is not taken into account. Some authors believe that this situation of rigidity overestimates the stress values, since the compliance of the tooth structure would prevent the development of such high stresses<sup>69,96</sup>. When a feedback system is not included in the testing apparatus, the shrinking composite is free to pull the rods together and the value registered is the result of the contraction force exerted by the material. In this case, the values registered are usually lower than those found using a feedback system<sup>9,21,47,69</sup>. Depending on the rigidity of the test set-up, the relationship between the stress and the ratio of bonded to unbonded surfaces of the composite specimen (C-factor) varies. In near-zero compliance set-ups, this relationship is direct<sup>22,37</sup>. An inverse relationship has been observed when non-rigid set-ups were used<sup>9,96</sup>.

Another important aspect of the contraction stress test is that only the forces developing uniaxially are registered. Due to the geometry and boundary restraints of the specimen, the distribution of forces in the specimen is rather complex. A finite element study verified that the forces developed during the contraction of the composite generate a triaxial stress state, due to the high aspect ratio of diameter to height of the specimens<sup>62</sup>. Therefore, the contraction values registered in the tensiometer represent only a fraction of the forces exerted by the shrinking material on the system. The thickness of the composite sample also affects the distribution of the stress. The findings of a study by Feilzer, et al.<sup>38</sup> suggested that in thin composite films, the contraction vector is strongly influenced by the boundary restraints. In fact, the above-mentioned study<sup>62</sup> verified that the end restraints affect the entire volume of the shrinking composite. Apparently, this effect is accentuated in thin layers, contributing to an inverse relationship between film thickness and contraction stress<sup>3</sup>.

A few studies have tried to correlate the results from contraction stress tests with those from microleakage tests. Choi, et al.<sup>22</sup> observed that the thickness of unfilled resin used to bond the composite to the glass in the tensiometer was inversely related to the contraction stress, and also caused a reduction in microleakage of class V cavities restored in one single increment. Another study<sup>15</sup> compared results of contraction stress test with microleakage in class I porcelain inlays placed in cavity preparations with margins in enamel. It was found that resin cements present higher contraction stress values and higher microleakage scores when tested in dual-cure mode

compared to self-cure mode. However, scanning electronic microscopy analysis was not able to detect differences in terms of percentage of interfacial gaps. A third study<sup>42</sup> verified a direct relationship between contraction stress and microleakage in class V cavities for three commercial restorative composites. It should be kept in mind that the values obtained from contraction stress tests represent the average of a heterogeneous stress distribution, while marginal gap formation is the result of a localized bond failure. Moreover, the analysis of sectioned specimens is very limiting, and may not be representative of the whole specimen. Therefore, the fact that some correlation between contraction stress and microleakage could be observed is a very positive indicator of the validity of the stress test method.

## POLYMERIZATION CONTRACTION STRESS OF CURRENT COMPOSITES

Studies evaluating the contraction stress of current commercial composites are summarized in the Table. Similar to other mechanical tests, the absolute value of the results from different contraction stress studies are hardly comparable. Besides differences in compliance of the testing set-ups, the dimensions of the composite sample, the period of force monitoring and the direction of photo-activation may also vary.

Nevertheless, with respect to the compositional characteristics of composites, it has been observed that microfill composites tend to develop lower contraction stress than hybrids<sup>9,17,28,64</sup>. According to Labella et al.,<sup>61</sup> microfilled composites present lower elastic modulus but similar volumetric shrinkage as hybrids, despite the lower filler content of the former. This apparent contradiction is explained by the presence of pre-polymerized filler particles in most of the microfilled composites, which serves to reduce the amount of resin matrix available to shrink. As a result, the contraction stress for microfills is generally smaller than that of more densely filled composites.

The contraction stress of packable composites has been evaluated by Chen, et al.<sup>21</sup>. All the five packable materials tested presented significantly higher stresses than the non-packable control. As the control material had a similar filler level as the packable composites tested, the authors suggested that rather than being correlated to the overall filler content, stress was related to the presence of large filler particles in the packable composites. It was supposed that these large fillers contributed to an increase in the elastic modulus compared to that of the control, resulting in higher contraction stress. It should be noted, however, that other studies have shown similar elastic

modulus and volumetric shrinkage for packable and non-packable composites<sup>23</sup>, emphasizing the importance of the choice of controls in such comparative studies.

Flowable composites present stress values similar to more densely-filled materials<sup>17</sup>. Their low filler content causes them to develop high volumetric shrinkage, approaching 6% in some products<sup>7,61</sup>. This, in spite of their low elastic modulus, seems to be main cause for their high contraction stresses. Clinically, this means that the risk of interfacial debonding for flowable and non-flowable composites due to shrinkage stress is similar. Nevertheless, the low elastic modulus of flowable composites may still be advantageous to maintain the interfacial integrity of the restoration when faced with different sources of stress<sup>58</sup>.

The contraction stress of resin cements has been measured by Braga, et al.<sup>15</sup>. Three dual-cure materials were evaluated in both dual-cure and self-cure-only modes. For all of the cements, the contraction stress in dual-cure mode (4.5 – 6.4 MPa) was higher than that in self-cure mode (3.4 - 4.0 MPa). The reduced stress in self-cure mode may have been the result of two concurrent factors. First, it is likely that there was a delay in stress build-up within the cements in self-cure mode due to a slower setting rate and a resultant extended flow and pre-gel shrinkage stage. Second, a lower degree of conversion of the cements in the absence of photo-activation<sup>16</sup> should result in a reduction in both the volumetric shrinkage and the elastic modulus of the material.

## INFLUENCE OF PHOTO-ACTIVATION METHODS ON CONTRACTION STRESS

As mentioned previously, the magnitude of the contraction stress is highly dependent on the composite's viscous component. Stress reduction by viscous flow may occur in two ways. First, the available free surface of the composite allows the material to deform when shrinking (external flow). Second, the longer it takes for the composite to develop a high elastic modulus, the more time is available for the polymeric chains to deform and slip into new positions to adjust to the shrinkage (internal flow), reducing or delaying contraction stresses build-up. In other words, if a higher proportion of the total volumetric contraction takes place while the composite remains in a non-rigid state, a smaller fraction of the shrinkage will effectively be responsible for stress development<sup>95</sup>.

To some extent, it is clinically possible to reduce the curing rate of a composite by lowering the intensity of the light used in the photo-activation. Conversion rate is proportional to the square root of the power density ( $PD = mW/cm^2$ )<sup>10</sup>. Alternative curing routines using stepped, pulsed or ramped energy delivery have been developed with the intent of improving the interfacial integrity of composite restorations by reducing the curing rate or the composites, and therefore, increasing its flow capacity<sup>24,50,56,91</sup>. However, in order to be effective, these new “soft

**TABLE-** Contraction stress of current composites

Study	Configuration Factor <sup>*</sup>	Feedback system <sup>**</sup>	Type of composite	Maximum Stress (MPa)
Bouschlicher et al. (1997) <sup>9</sup>	C = 3	no	Hybrid	4.6
			Microfill	3.4
Condon and Ferracane (2000) <sup>28</sup>	C = 1	yes	Hybrid	5.5 – 7.0
			Microfill	4.0 – 4.5
Chen et al. (2001) <sup>21</sup>	C = 0.33	no	Hybrid	2.5
			Packable	3.3 – 4.6
Lim et al. (2002) <sup>64</sup>	C = 3	yes	Hybrid	8.8 – 12.5
			Microfill	7.7
Watts et al. (2003) <sup>96</sup>	C = 4.16	no	Hybrid	5.4 – 7.8
	C = 6.25			4.9 – 7.0
Braga et al. (2003) <sup>17</sup>	C = 3	yes	Hybrid	7.4 – 9.0
			Microfill	6.1
			Flowable	6.0 – 9.1

\*ratio of bonded to unbonded surfaces of the composite

\*\*indicates the use of a near-zero compliance set-up.



start” curing methods should be able to significantly reduce contraction stress and improve marginal integrity, and without compromising the composite’s degree of conversion or its mechanical properties.

Studies evaluating alternative curing routines in terms of contraction stress are few. Bouschlicher and Rueggeberg<sup>10</sup> evaluated one light unit (Trilight, 3M ESPE) and found lower contraction forces (approximately 33%), lower curing rate (approximately 20%) and similar degree of conversion for ramped curing compared to a continuous light activation. In the same study, the use of a stepped curing mode (Highlight, 3M ESPE) did not significantly reduce the contraction force. Lim, et al.<sup>64</sup> verified stress reductions between 19% and 30% for three different composites when a two-step curing technique was compared to a continuous light exposure with equivalent energy density. Both methods allowed similar degrees of conversion. According to the authors, when a two-step curing routine is adopted, three aspects should be observed, namely, the initial light intensity, the exposure time of the initial low-intensity irradiation, and the time interval between the two irradiations.

Marginal integrity studies on “soft start” polymerization show contradictory results. While some studies showed improved marginal integrity with non-continuous curing methods<sup>66,68</sup>, others did not find significant differences between those and conventional (continuous) curing<sup>43,79</sup>. One aspect that remains unclear is the effect of a non-continuous irradiation on the polymer structure. It has been hypothesized that low curing rates may originate longer polymeric chains and less cross-linking, affecting the mechanical properties of the polymer<sup>5</sup>. However, others have characterized the structure and properties of cross-linked dimethacrylate polymers cured at low and high conversion rates, and found no significant difference in properties or overall conversion<sup>65</sup>.

Besides the curing rate, another aspect related to photo-activation that affects contraction stress is the total energy delivered to the composite ( $ED = PD \times \text{time} = mW \times s/cm^2 = mJ/cm^2$ ). The use of high energy densities to cure composites has been associated with superior mechanical properties and degree of conversion<sup>77</sup>. The relationship between energy density and degree of conversion, however, is not linear<sup>80</sup>. In other words, there is a limit where higher energy levels do not correspond to significant increases in degree of conversion or mechanical properties<sup>87</sup>. Unfortunately, the relationship between energy density and post-gel shrinkage strain was found to be linear<sup>80,84</sup>. Therefore, high energy densities translate into higher stress levels, but do not necessarily result in high degrees of

conversion or superior mechanical properties.

The relationship between degree of conversion (DC) and contraction stress seems to be more complex. Apparently, there is a threshold in the DC above which non-significant increases correspond to significantly higher stress levels<sup>14</sup>. Clinically, it is almost impossible to determine which energy level would provide the best relationship between degree of conversion, mechanical properties and contraction stress. Still, it is important to keep in mind that over-exposing the composite to photo-activation might increase the risk of marginal and interfacial debonding, as well a heat buildup within the tooth.

### THE USE OF LOW ELASTIC MODULUS LINERS AS STRESS-ABSORBING LAYERS

The magnitude of the stresses developed at the restoration’s interface is related to the compliance of the surrounding structures. If the substrate to which the shrinking composite is bonded can yield to contraction forces, the developed stress is lower<sup>4</sup>. The application of a low elastic modulus material to the cavity walls represents a way to artificially increase the compliance of the prepared cavity. Besides the elastic modulus of the liner, the thickness of the applied layer may also influence the stress relief. The thicker the layer, the better are the chances of a significant stress relief<sup>92</sup>. Finite element analysis studies support this idea<sup>6,76</sup>.

Kemp-Scholte and Davidson<sup>57</sup> observed that the use of a 150  $\mu\text{m}$  layer of unfilled resin under a bulk-cured layer of a high modulus composite significantly improved marginal sealing of class V restorations and significantly reduced stress values. More recently, Choi, et al.<sup>22</sup> verified that the application of layers of unfilled resin in the range of 100 to 200  $\mu\text{m}$  reduced contraction stress between 13 and 24% and significantly reduced microleakage in class V cavities. However, as noted by the authors, the clinical use of unfilled resin in thick layers is problematic. First, the material is radiolucent, what would preclude radiographic diagnosis and, second, the fluidity of the material would make the application somewhat difficult in some areas of the cavity.

The use of low-viscosity (“flowable”) composites as stress-absorbing layer material has been advocated by many authors<sup>8,53,92</sup>. In general, flowable composites have lower elastic moduli than more densely-filled materials<sup>61,74,78</sup>. However, the results of microleakage studies conducted *in vitro* are contradictory. While some authors reported lower microleakage with the use of a pre-polymerized layer of flowable

composite<sup>54,73,98</sup>, others were not able to detect any improvement in marginal integrity<sup>63,97</sup>. Besides differences in layer thickness among studies, a possible explanation for this inconsistency is the broad range of elastic modulus values displayed by flowable composites. Labella, et al.<sup>61</sup> reported values between 6.5 and 12.5 GPa for 12 different flowable composites. For comparison purposes, in the same study, the elastic modulus of an unfilled Bis-GMA resin was 4.6 GPa. Sabbagh, et al.<sup>78</sup> reported values ranging between 1.4 and 4.4 GPa for five low-viscosity materials.

A previous study<sup>17</sup> verified the influence of the elastic modulus of a pre-cured composite layer on the contraction stress developed by a subsequent layer of densely-filled composite. Four flowable composites were evaluated, with elastic moduli ranging between 4.1 and 8.2 GPa. An unfilled resin (elastic modulus: 2.1 GPa) was also included in the study. In spite of the high thickness of the pre-cured layer used in the study (1.4 mm), a large and significant stress relief (approximately 41%) was observed only with the unfilled resin as the pre-cured material when compared to the value obtained with a pre-cured layer built with a densely-filled composite (elastic modulus: 12.3 GPa). Only one of the flowable composites allowed a potentially significant stress relief (approximately 19%).

### STRATEGIES FOR STRESS REDUCTION IN EXPERIMENTAL BIS-GMA-BASED COMPOSITES

Modifications to the basic components of composites have been proposed in order to reduce contraction stress development. The general idea is to increase the opportunity for stress relief by flow, since the monomers present are the same found in the currently commercial composites and, therefore, the same levels of volumetric shrinkage are expected.

The use of non-bonded nanofillers (40 nm colloidal silica) was tested as an alternative to provide internal sites for stress relief without compromising the mechanical properties of the composite<sup>27</sup>. In the experimental nanofilled composite, close to 50% reduction in stress was observed when non-functional silane-treated particles were added compared to the control material containing particles with a functional (methacrylate) silane. The experimental hybrid composite produced 31% less stress when non-silanated nanofill particles were added. Though it was not directly observed, the proposed mechanism of stress relief was that the non-bonded nanofillers would allow the resin matrix to flow around them and react without constraint, similar to the mechanism proposed

for the stress reduction in unfilled resins with admixed porosity<sup>2</sup>. No reductions in flexural modulus, degree of conversion or fracture toughness were observed in these experimental materials<sup>48</sup>. A recent study<sup>29</sup> further investigated the effect of non-bonded nanofiller and verified that the optimal non-bonded nanofiller content was independent of the presence of filler particles of different sizes.

The effect of increased inhibitor concentrations (BHT, butylated hydroxytoluene) on contraction stress, degree of conversion and volumetric shrinkage has also been evaluated<sup>14</sup>. A significant stress reduction (approximately 39%) was observed when the BHT concentration was increased from 0.05% (by weight) to 1.0%. The inhibitor molecules react with the free radicals generated by photo-activation, and polymerization proceeds at a reduced rate until the inhibitor is completely consumed. This effectively extends the pre-gel phase. Intermediate inhibitor concentrations caused significant reductions in curing rate, but not in contraction stress, suggesting that the reaction speed must be reduced below a certain threshold in order to significantly reduce contraction stress. Degree of conversion and volumetric shrinkage were not significantly affected. However, further studies are necessary to verify whether composites with high inhibitor concentrations have adequate mechanical properties.

The addition of high-density polyethylene spheres (HDPE) to hybrid and nanofilled experimental composites has also been verified as a stress relief mechanism<sup>41</sup>. In both cases, the addition of 20 wt% of HDPE spheres led to significant stress reductions compared to the respective control groups (between 26% and 29%). In the hybrid composite, the polyethylene spheres replaced the filler and the stress reduction seemed to be related to a reduction in elastic modulus. In the nanofilled composite, the spheres were added to the control material, without altering the resin-to-filler ratio. In that case, the stress reduction was associated to a reduction in volumetric shrinkage. However, a general trend for lower mechanical properties with increased HDPE levels was observed, most noticeably with the hybrid materials.

### RECENT DEVELOPMENTS IN LOW SHRINKAGE MONOMERS

Several approaches have been pursued in the past to reduce polymerization shrinkage in dental resins. Expanding monomers based on spiroorthocarbonates (SOC) were first attempted for dental composites, but the materials were not successfully commercialized<sup>89</sup>.

The addition of SOCs to dimethacrylate resins cured by free radical polymerization<sup>85</sup> and to epoxy resins cured by cationic polymerization<sup>19,36</sup> have both been attempted within the past 10 years. Though studies showed lower shrinkage and subsequently lower shrinkage stress with the epoxy-based systems, it is likely that the reductions are related to the lower overall conversion of monomer to polymer in these systems<sup>20</sup>. The radical ring opening approach using unsaturated spiroorthocarbonates or vinylcyclopropanes (VCP) has been also pursued to reduce shrinkage in composites<sup>70,71</sup>. Though no commercial product has been realized from these approaches to date, work is continuing.

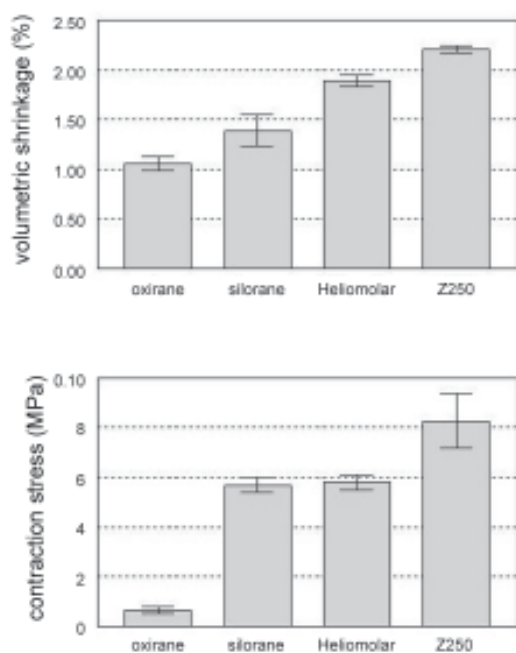
Cycloaliphatic epoxy resins (also called oxiranes), formulated with polyols, such as polytetrahydrofuran, have been investigated and proposed as photocurable, cationic polymerized resins for dental composites with nearly one-half of the polymerization shrinkage of Bis-GMA-based resins<sup>90</sup>. These resins also have the advantage of no air-inhibited layer and high strength, but relatively high water sorption. Guggenberger and Weinmann<sup>44</sup> recently discussed similar alternatives to dimethacrylates for dental composite matrices. They described a family of molecules called siloranes, the name being derived from the combination of siloxanes and oxiranes (epoxies). These molecules polymerize by cationic photoinitiation and produce dental composites with comparable properties and slightly

reduced shrinkage compared to Bis-GMA-based materials. We have evaluated some of the properties of silorane and oxirane-based composites and have verified that they do in fact have lower volumetric shrinkage and lower contraction stress than commercial Bis-GMA-based composites (Figure 2).

Culbertson, et al.<sup>30,31</sup> have synthesized esterified multi-methacrylate oligomers of poly (isopropylidenediphenol) (BPA) and mixed them with TEGDMA to produce resins with a 10-15% reduction in polymerization shrinkage compared to Bis-GMA-based resins. However, these new resins did not cure as well as the Bis-GMA-based resins, and this again is the likely reason for their lower contraction. The contraction stress of these materials has not been tested, but due to their greater rigidity than Bis-GMA, it is doubtful that they would have lower shrinkage stress.

Interesting bismethacrylates with lower shrinkage than Bis-GMA have been produced by Holter, et al.<sup>51</sup> by reacting various branching molecules at the hydroxy groups of the Bis-GMA. However, initial results suggest that these polymers have a low elastic modulus. While this low modulus and lower shrinkage would likely result in lower contraction stress than Bis-GMA-based polymers, the low modulus (50% of Bis-GMA-based resins) may limit their usefulness as dental restorative resins. In other studies, Chung, et al.<sup>25,26</sup> developed new trimethacrylate monomers (1,1,1-Tris[4-(2'-hydroxy-3'-methacryloxyloxypropoxy) phenyl]ethane (and methane) that produced composites with slightly reduced polymerization shrinkage and water sorption than Bis-GMA-based composites, and with similar conversion and flexural strength.

Other approaches proposed for reducing polymerization contraction in dental composites include the development of liquid crystal monomers<sup>75</sup> and cyclopolymerizable di- and multi-functional acrylate resins<sup>86</sup>. Culbertson, et al.<sup>32</sup> presented the synthesis of a methacrylated derivative of styrene-allyl alcohol, MSAA, to be used as a comonomer for dental composites to improve strength and conversion. In one study, MSAA was used to replace 20% of the Bis-GMA in a highly filled Bis-GMA/TEGDMA composite and showed a 20% reduction in polymerization contraction stress<sup>28</sup>. The addition of large amounts of MSAA has a significant negative effect on mechanical properties, however.



**FIGURE 2-** Volumetric shrinkage (top) and contraction stress (bottom) of an oxirane- and a silorane-based composite compared to two commercial composites

## CONCLUSION

Polymerization contraction stress has been the subject of intense research activity over the last few years. Though most of the factors involved in stress development have been identified, further studies are necessary to access the individual contributions of the composite's physical properties (namely, volumetric shrinkage and elastic modulus) and curing kinetics (as a factor determining stress relief by viscous flow), and potential interactions between them. Some of the proposed non-continuous curing routines have been shown to significantly reduce contraction stress. However, results of interfacial integrity studies are inconsistent and, in some cases, stress reduction might be caused by a lower degree of conversion. Stress reduction with the use of low elastic modulus liners seems to require materials with stiffness close to that of unfilled resins. Apparently, many of the flowable composites currently available are too rigid to be used for this purpose. Developing low-shrinkage monomers that could match other clinically important properties found in Bis-GMA-based composites is a challenging task. Nevertheless, some studies have shown promising results regarding contraction stress reduction.

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