Role of Composition on Polymerization Shrinkage and Shrinkage Stress in Dental Composites

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ABSTRACT

Polymer-based dental composites are the widely used direct restorative materials. However, one of the disadvantages that include polymerization shrinkage, which leads to a cascade of effects like shrinkage stress, cusp deflection, enamel/dentin cracks, marginal leakage, marginal discoloration, secondary caries, and postoperative sensitivity, needs eradication to improvise their performance. Polymerization shrinkage is the result of covalent bonds replacing van der Waals forces in a polymer. Many factors play a significant role in the polymerization shrinkage development, its magnitude, and the shrinkage stress. Viscosity, glass transition temperature, density, reaction kinetics, molecular mobility, modulus development, gel point, vitrification, degree of conversion, configuration (C) factor, and compliance of bonded surfaces dictate both the quantum of shrinkage and when it occurs and if and how its stresses are relieved. There are three efficient methods of reducing polymerization shrinkage and shrinkage stress. The first one focuses on reducing the reactive groups, the second one focuses on introducing new chemistries, and the third method focuses on controlling curing protocols. Increasing the molar volume and molecular weight of resins helps reduce reactive groups as is increasing the filler content. Alternative polymerization methods like ring-opening polymerization and step-growth polymerization have been very effective ways of reducing shrinkage. Debonding the fillers or using functionalized fillers or using different coupling agents based on chain transfer and dynamic covalent chemistry (DCC) are promising methods to relieve shrinkage stress. Modifying the available methacrylates; introducing certain chemicals; altering solvents, inhibitors, initiators, and coinitiators; using bulk-fill concept; and utilizing ormocer technology are also catching up with moderate to immense potential to reduce either shrinkage or shrinkage stress. Among filler modifications, nanogel incorporation, among matrix modifications, thio-carbonate and ally sulfide introduction and among coupling agent modifications, using functionalized agents seem to be the best methods in either reducing shrinkage or shrinkage stress. Though laboratory investigations have been very much encouraging the above-mentioned methods, the real test of clinical studies is not as optimistic. Long-term clinical performance of materials based on these various methods has not been clinically significantly different from conventional materials. Nonetheless, some of the new materials have not yet gone through the rigorous of long-term clinical studies and hence controlled clinical trials of such materials are highly recommended.

Keywords: Bulk-fill composites, Composite resin, Methacrylates, Ormocers, Polymerization shrinkage, Shrinkage stress, Silorane, Thiol-ene.

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INTRODUCTION

Dental composites have been rehabilitating many teeth and smiles since their inception seven decades back. Ever since the introduction of acid-etching by Michael Buonocore in 1955 and Bisphenol A diglycidyl methacrylate (BisGMA) resin by Bowen in 1960, composites have been the most popular direct aesthetic restorative materials available to dentists.

Polymerization shrinkage is defined as the volumetric contraction of polymers as opposed to monomers upon polymerization reaction that hardens the resin. In general and also in dental composites, it is caused by the replacement of loose van der Waals bonds in the monomeric resin by the compact covalent bonds in a polymeric resin. In conventional and contemporary composites, it ranges between 1 and 6%. Conventional composites utilize free-radical addition polymerization (Fig. 1), and methacrylate chemistry is the most often utilized in resin (Fig. 2). Even though ormocers were introduced to reduce shrinkage, they too polymerize by free-radical polymerization. The three popular methods of reducing shrinkage are as follows:

(I) Reducing reactive sites
   A) By increasing molecular weight/unit volume of resin/reducing double-bond concentration of resins
   B) By increasing filler

(II) Introducing new chemistries

A) Alternative polymerization techniques
   1) Ring-opening polymerization
      a) Liquid crystalline monomers (Fig. 3)
      b) Vinyl cyclopropane (Fig. 4)
      c) Spiro-orthocarbonate (Fig. 5)
      d) Siloranes (Fig. 6)
   2) Step-growth polymerization
      a) Thiol-Michael
      b) Thio-urethanes
      c) Thiol-ene
      d) Thio-carbonate

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Fig. 1: Free-radical addition polymerization (Source: From Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. Dent Mater 2005;21(1):68–74. DOI: 10.1016/j.dental.2004.10.007.)

Fig. 2: Commonly used dimethacrylates in dental composites (Source: From Charton C, Falk V, Marchal P, et al. Influence of $T_g$, viscosity and chemical structure of monomers on shrinkage stress in light-cured dimethacrylate-based dental resins. Dent Mater 2007;23(11):1447–1459. DOI: 10.1016/j.dental.2007.05.017.)

Fig. 3: Liquid crystal monomer (Source: From Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. Dent Mater 2005;21(1):68–74. DOI: 10.1016/j.dental.2004.10.007.)
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![Vinyl cyclopropane](image)

Fig. 4: Vinyl cyclopropane (Source: From Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. Dent Mater 2005;21(1):68–74. DOI: 10.1016/j.dental.2004.10.007.)

![Spiro-orthocarbonate](image)

Fig. 5: Spiro-orthocarbonate (Source: From Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. Dent Mater 2005;21(1):68–74. DOI: 10.1016/j.dental.2004.10.007.)

![Silorane](image)

Fig. 6: Silorane (Source: From Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. Dent Mater 2005;21(1):68–74. DOI: 10.1016/j.dental.2004.10.007.)

B) Other compositional modifications

1) Modification of coupling agents
2) Modifying dimethacrylate formulations
3) Alternative photoinitiators
4) Alternative coinitiators/accelerators
5) Bulk-fill concept
6) Ormocers

III) Alternative curing protocols

A) Irradiance control
B) Placement techniques
C) Curing methods.

This review will focus on the first two methods of reducing polymerization shrinkage which are dependent on the composition.

Patel et al. found that on average, 22.5 cm$^3$ volumetric reduction occurred per double bond in esteric methacrylates upon polymerization. Hence, molar volume increase is an attractive option to negate shrinkage.

While many strategies are explored to reduce or compensate for polymerization shrinkage in composites, the first two strategies prove to address the primary problem, while the third is designed to counter the effects of the same, namely polymerization shrinkage stress. The different compositional modifications can be subclassified as those pertaining to matrixes, fillers, coupling agents, initiators, and others (Fig. 7). Modifications in resin chemistry also include isobornyl acrylates. Factors other than chemistries affecting shrinkage behavior are the rate and extent of polymerization, degree of conversion or DC, and modulus of elasticity of the polymerized matrices. These factors help in reducing the shrinkage stresses.

**Etiology and Effects**

During the polymerization of vinyl polymers, two processes happen to increase shrinkage, namely increase in density and decrease in mobility. In the last five decades, monomers and fillers have been extensively researched and modified to negate polymerization...
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Fig. 7: Factors that can reduce polymerization shrinkage and/or shrinkage stress (Source: From Meereis CTW, Münchow EA, Oliveira da Rosa WL, et al. Polymerization shrinkage stress of resin-based dental materials: a systematic review and metaanalyses of composition strategies. J Mech Behav Biomed Mater 2018;82:268–281. DOI: 10.1016/j.jmbbm.2018.03.019.)

shrinkage. However, clinically lower shrinkage values do not always translate as less interfacial gaps or beneficial. In studies, it has been shown that low-shrinking monomers show less stress with low C factor while demonstrating more stress with high C factor. Calheiros et al. demonstrated that commercial low-shrink materials Aelite and In Ten S have greater stress and microleakage than regular hybrids.\(^6\)\(^7\) This is due to the fact that shrinkage is but only one factor among the multitude of factors responsible for shrinkage stress that is clinically more relevant, others being vitrification, elastic modulus, reaction rate, C-factor, and compliance of bonded surfaces. Compliance is a clinical phenomenon, which is affected by cavity geometry and stiffness of the remaining tooth structure.\(^6\) The time-dependent viscous flow of composites affects their plastic deformation that in turn impacts shrinkage stress relief. During the initial stages of polymerization, cyclization and chain growth are prioritized over cross-linking. Hence, interchain covalent bonds do not form and plastic deformation is ensured. It is the “rigid contraction” or postgel shrinkage that produces stress. Molecular resistance to flow is indicated by viscosity while monomeric flexibility is indicated by glass transition temperature (\(T_g\)). Together, they govern the molecular mobility of resins.\(^7\)

**METHODS OF REDUCING POLYMERIZATION SHRINKAGE AND SHRINKAGE STRESS**

**Reducing Reactive Sites**

*Increasing Molecular Weight/Unit Volume of Resin/Reducing Double-bond Concentration of Resins*

One of the popular methods of reducing shrinkage includes altering reactive group concentration.\(^9\)\(^10\)

Reactive group concentration can be reduced by using monomers with less double-bond concentration, thus decreasing polymerization shrinkage. Silsesquioxanes are popular in this category, especially the polyhedral oligomeric silsesquioxane (POSS). It has been proven to increase molecular weight and decrease double-bond concentration. Bisphenol A ethoxy fluorene methacrylate (BisEFMA) (Fig. 8) with higher molecular weight than conventional dimethacrylates was found to have the lowest shrinkage in a study.\(^11\) Multifunctionality decreases shrinkage without compromising mechanical properties. Introducing bulky substituent groups can increase molecular weight, molar volume, and decrease reactive double bonds. Mono-tertiary butyl and di-tertiary butyl groups can be added to methacrylate (Fig. 9) by ring-opening polymerization of the diepoxide with the corresponding phenol and reacting with methacrylic anhydride.\(^12\) DX-511 is a modified

![Fig. 8: Bisphenol A ethoxy fluorene methacrylate (Source: From He J, Kopperud HM. Preparation and characterization of BisGMA-free dental composites with dimethacrylate monomer derived from 9,9-Bis[4-(2-hydroxyethoxy)phenyl]fluorene. Dent Mater 2018;34(7):1003. DOI: 10.1016/j.dental.2018.03.007.)](image-url)
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Resin matrix by physical entanglement or chemical means. Further, they delay modulus development and vitrification. Reactive organic nanogel prepolymer additives achieved less stress without light attenuation. Reactive organic nanogel prepolymer slow down reaction rate to reduce shrinkage. In a systematic review, the authors studied the role of fillers and other components on polymerization shrinkage and shrinkage stress reduction; 62 laboratory studies were qualitatively synthesized, and 58 quantitatively. They found that the fillers had a range of 2–59% in reducing the stress, and nanogel incorporation was found to be the best method among the fillers’ modifications.

Introducing New Chemistries
Alternative Polymerization

Ring-opening polymerization: Ring-opening polymerization has the unique advantage of volumetric gain due to the reverse situation, of a closed ring in a monomer occupying less space than the open ring in a polymer, as against the linear molecule of conventional resins.

High inorganic filler content increases stiffness and also shrinkage stress. High-density polyethylene (HDPE) spheres are substituted in part for stiff fillers to counteract this. A 20% of addition resulted in 25% of reduction of stress. However, crucial mechanical properties may be compromised in such materials. Cross-linked polymeric nanoparticles have been shown to reduce shrinkage by 7–30%, stress from 2–18% when added in the range of 5–25%. E-glass fibers that have similar modulus and stiffness of particulate glass fillers were found to relieve stress by 5% due to increased compliance.

Nanogels are single- or multichain polymeric particles that are cyclized and cross-linked internally, which allows cross-linking of the resin matrix by physical entanglement or chemical means. Further, they delay modulus development and vitrification. Reactive nanogel prepolymer additives achieved less stress without light attenuation. Reactive organic nanogel prepolymer slow down reaction rate to reduce shrinkage. In a systematic review, the authors studied the role of fillers and other components on polymerization shrinkage and shrinkage stress reduction; 62 laboratory studies were qualitatively synthesized, and 58 quantitatively. They found that the fillers had a range of 2–59% in reducing the stress, and nanogel incorporation was found to be the best method among the fillers’ modifications.

Increasing Filler

Though resin matrix is primarily responsible for shrinkage, fillers also play a role. Though conventional wisdom has shown that filler loading reduces polymerization shrinkage, the higher it is, the greater is the light scattering, which hinders photopolymerization, and the greater is the viscosity, and few studies indicate that lower filler volume gives rise to low shrinkage and shrinkage stress. Both filler content and size play a major role in affecting shrinkage and shrinkage stress. It was found that even a 5% increase in filler content significantly reduced shrinkage stress. Also, a positive correlation between filler size and stress reduction was especially noticed for spherical fillers. This is due to more translational and rotational movement within the resin matrix. However, since contemporary dental composites rely more on nanofillers for optical properties and aesthetics, this above-mentioned phenomenon is immaterial. In addition to the polymerization shrinkage and shrinkage stress, thermal expansion mismatch and modulus mismatch between fillers and resins result in additional stresses.

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Liquid crystalline monomers undergo a transition of their nematic phase to an isotropic amorphous state resulting in reduced shrinkage. Vinyl cyclopropanes undergo ring-opening polymerization via radicals. They can be copolymerized with methacrylates. Free-radical ring-opening polymerization of spiro-orthoesters, carbonates, and cyclic acrylates increases their molar volume. Spiro-orthocarbonates undergo ring-opening polymerization via cation (Fig. 10). Their expansion potential was first elucidated by Bailey in 1975. Thompson investigated their use in dentistry in 1979. On average, they show 3–4% of expansion particularly with the tetraoxaspiro-undecane (TOSU) type of spiro-orthocarbonates, based on the cis or trans isomer (Fig. 11) is used. They have the ability to reduce shrinkage stress from 48–99%. They reduce modulus during polymerization, glass transition temperature, reaction rate and hence increase...
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Fig. 12: Cationic photo initiators (Source: From Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. Dent Mater 2005;21(1):68–74. DOI: 10.1016/j.dental.2004.10.007.)

Photoinitiation: P → P

Propagation: RS⁻ R’CH=CH₂ → R’C⁺H⁻CH₂SR

Reaction with O₂: RC⁺H⁻CH₂SR + O₂ → R’CH⁻CH₂SR + RS⁻

Termination: 2 RS⁻ R-S-S-R

Another method of decreasing shrinkage is by delaying gel point. This is achieved through thiol-Michael step-growth polymerization (Fig. 13). Yet another category of materials with delayed gelation are thio-urethanes. Oligomers with pendant thiol groups undergo chain transfer with methacrylate to delay vitrification. This relieves stresses. One such material was synthesized from 4,4-methylene bis(cyclohexyl isocyanate), trimethyl-tris-3-mercaptopropionate, and 3-(triethoxysilyl)propyl isocyanate with triethylamine as catalyst. Thio-urethanes have greater toughness and chemical stability and also have a potential to reduce shrinkage stress from 10–88%. Among the step-growth polymers, they were found to be the best in reducing shrinkage stress in a systematic review cum meta-analyses. Posner was the first person to discover the thiol-ene polymerization. The advantages include nearly complete consumption of all reactive groups, improved depth of cure and flexibility. Thiol-ene polymerization has shown a significant reduction in shrinkage stress in many studies. The thiol (PETMP) and the ene, a triallyl ether, triallyl trizine trione (TATATO) combination (Fig. 15) showed 86% of reduction in stress. In step-growth polymerization, the scope for stress relief is more. Here, a thiol radical gets added to an ene molecule and a chain transfer occurs to a thiol group freeing the thyl radical again (Fig. 13). Apart from the rapid rate, they are also insensitive to O₂ inhibition. Upon combining with methacrylates, there is homopolymerization of methacrylates initially, followed by thiol-ene step-growth later. However, if thiol ratio is less, conversion will be low. To offset this, more thiolen has to be added. This has a downside of producing a bad odor. This problem can, however, be controlled to some extent by using high molecular weight thiols like tetrafunctional thiol monomer. Upon further mixing with methacrylates and fillers, the odor disappears. The advantage of any thiol is that they act as diluent and an electron donor as redox (Fig. 12). Counteranions in acid generator iodonium salt as acid generator, camphorquinone (CQ) as photosensitizer, and an electron donor as redox (Fig. 12). Counteranions in acid generator iodonium salt like antimonate increase the reactivity. Siloranes were found to have less than 1% of final shrinkage that is probably one of the lowest known for hitherto forc. They have been found to reduce stress by 97% in many studies and were found to increase flow in the pre-gelation phase; nonetheless, some studies found them to be not beneficial in reducing stress. Siloranes are available commercially as Filtek P90, Filtek Silorane P90, and FiltekLSLow Shrink. In a recent systematic review cum meta-analyses, Magno and others reviewed 11 clinical studies comparing silorane to methacrylates and concluded that they performed clinically equal without any significant difference.

Step-growth Polymerization: Another method of decreasing shrinkage is by delaying gel point. This is achieved through thiol-Michael step-growth polymerization (Fig. 13). Yet another category of materials with delayed gelation are thio-urethanes. Oligomers with pendant thiol groups undergo chain transfer with methacrylate to delay vitrification. This relieves stresses.

Fig. 13: Step-growth polymerization (Source: From Lu H, Carioscia JA, Stansbury JW, et al. Investigations of step-growth thiol-ene polymerizations for novel dental restoratives. Dent Mater 2005;21(12):1129–1136. DOI: 10.1016/j.dental.2005.04.001.)

**Fig. 13:** 2,3,8,9-Ditetramethylene-1,5,7,11 tetraoxaspiro-5,5 undecane (TOSU) and its isomers (Source: From Byerley TJ, Eick JD, Chen GP, et al. Synthesis and polymerization of new expanding dental monomers. Dent Mater 1992;8(6):345–350. DOI: 10.1016/0109-5641(92)90016-6.)
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**Fig. 14:** Commonly used thiol in step-growth polymerization pentaerythritol tetramercaptopropionate (PETMP) (Source: From Cramer NB, Stanbury JW, Bowman CN. Recent advances and developments in composite dental restorative materials. J Dent Res 2011;90(4):402–416. DOI: 10.1177/0022034510381263.)

**Fig. 15:** Commonly used triallyl ether “ene” in thiol-ene polymerization triallyl triazine trione (TATATO) (Source: From Cramer NB, Stanbury JW, Bowman CN. Recent advances and developments in composite dental restorative materials. J Dent Res 2011;90(4):402–416. DOI: 10.1177/0022034510381263.)

**Fig. 16:** Commonly used norbornene “ene” in thiol-ene polymerization trimethylolpropanetinorbornene carboxylate (Source: From Cramer NB, Stanbury JW, Bowman CN. Recent advances and developments in composite dental restorative materials. J Dent Res 2011;90(4):402–416. DOI: 10.1177/0022034510381263.)

Potential in doing so, according to a recent systematic review cum meta-analyses of in vitro studies.

In resins, nonreactive prepolymers and marginally compatible comonomers relieve stress (Fig. 18) by polymerization-induced phase separation (PIPS). Hydrogenated dimer acids have high molecular weight and hence low shrinkage. Dimer acid derivate, dimer dicarbamate dimethacrylate is a low-shrinking high molecular weight monomer that uses PIPS to reduce shrinkage and shrinkage stress. Commercially, it is available as N’Durance.

**Other Compositional Modifications**

**Modification of Coupling Agents**

Nonfunctional silane-treated fillers produced less stress without compromising conversion unlike functional fillers. Oligomerization involves prereacting functionalities to reduce reactive species concentration. Alternative functionalization of fillers had a greater ability to reduce shrinkage stress than nonbonded, nonsilanized, and silane-treated fillers. Nonbonding and nonsilanization also improved rotational and translational movement of fillers to reduce stress. But mechanical properties could be compromised by this method. Nonfunctional fillers decrease chemical interaction with resin, to improve compliance. Further, the nonfunctional silane favored pregelation contraction. These filler types do not affect mechanical properties. Among functionalized fillers, flexible hyperbranched oligomer functionalized fillers and thiol functionalized fillers substantially reduce stress. This is due to the enhanced mobility of molecules. They also lower the modulus. Overall, any modification of coupling agent was able to reduce stress from 8–46% much lower than filler and very much lower than the resin matrix modifications.

Dynamic bond exchange of DCC facilitates relieving stresses from polymerization reaction and external loading while preserving overall covalent bonded structure in polymeric backbone. This is possible through reversible addition fragmentation chain transfer (RAFT). However, it can negatively impact Young’s modulus, glass transition, and fracture toughness. Precisely targeting the filler...
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A. Dynamic Covalent Chemistries (DCCs)

B. Bulk DCC and Interfacial DCC

C. Material Formulations

Fig. 19A to C: Dynamic covalent chemistry and reversible addition fragmentation chain transfer (Source: From Sowan N, Dobson A, Podgorski M, et al. Dynamic covalent chemistry (DCC) in dental restorative materials: implementation of a DCC-based adaptive interface (AI) at the resin–filler interface for improved performance. Dent Mater 2020;36(1):53–59. DOI: 10.1016/j.dental.2019.11.021.)

Fig. 20: Methylene propane dithioethyl vinyl ether (left) based on addition fragmentation chain transfer (AFCT); triethylene glycol divinyl ether (right) not based on AFCT (Source: From Sowan N, Dobson A, Podgorski M, et al. Dynamic covalent chemistry (DCC) in dental restorative materials: implementation of a DCC-based adaptive interface (AI) at the resin–filler interface for improved performance. Dent Mater 2020;36(1):53–59. DOI: 10.1016/j.dental.2019.11.021.)

particle–resin interface with this DCC could be more beneficial without impacting the mechanical properties. RAFCT-adaptive interface can relieve stress even in inert thiol-ene composite. A modification of this is thiol-thioester DCC moieties (Fig. 19) in conventional resin composite that is active even after light withdrawal as it is based on base-nucleophile catalyst. Further, a thiol radical is not required for bond exchange and hence is compatible with multimethacrylate composites. This is carried out by functionalizing silica nanoparticles with TTE silane and along with a nucleophile, introduction into a BisGMA–triethylene glycol dimethacrylate (TEGDMA) composite. A continuous bond cleavage happens with reversible reformation that relieves polymerization shrinkage stresses. Two DCC approaches are there, one in resin using RAFCT and the other at the interface using TTE; they act synergistically to improve mechanical properties and relieve stresses. In composites, bulk shrinkage stresses are responsible for failures by causing microcracks and debonding. Thus, composites with only filler–resin interface modification were found to have 30% of lower polymerization shrinkage stresses, double that Young’s modulus, 30% of more flexural strength, and 25% of more flexural toughness compared to conventional composites. These composites contain a divinyl addition fragmentation chain transfer (AFCT) [2-methylenepropane-1,3-dithioethyl vinyl ether (MDTVE)] or non-AFCT [triethylene glycol divinylether (TEGDVE)] (Fig. 20) and PETMP, with TTE-based fillers in the presence of nucleophile catalyst 1,4 diazabicyclo 2,2,2 octane (DABCO). If both resins and fillers are modified, 90% of reduction in stress is observed.

Modifying Dimethacrylates

Modifying dimethacrylate formulations is an equally promising area of research in reducing polymerization shrinkage and shrinkage stress.

Ethoxylated methacrylates and hyperbranched methacrylates have high molecular weight and hence demonstrate low shrinkage. Trifunctional monomers, like triphenylmethane triglycidyl ether methacrylate (TTEMA) (Fig. 21) shrunk less at only 2% compared...
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Fig. 21: Tris triphenylmethane glycidyl ether methacrylate (TTEMA) (Source: From Chung CM, Kim JG, Kim MS, et al. Development of a new photocurable composite resin with reduced curing shrinkage. Dent Mater 2002;18(2):174–178. DOI: 10.1016/s0109-5641(01)0039-2.)

Fig. 22: N-methyl bis ethyl-carbamate-isopropyl-methylstyryl amine (phene) (Source: From He J, Garoushi S, Säilynoja E, et al. The effect of adding a new monomer “Phene” on the polymerization shrinkage reduction of a dental resin composite. Dent Mater 2019;35(4):627–635. DOI: 10.1016/j.dental.2019.02.006.)

to BisGMA, TEGDMA, and UDMA which shrank by 5, 14, and 9%, respectively. When combining with TEGDMA at 3:2 ratio, a 10% of reduction was noted.

Chain transfer agents increase mobility to achieve low shrinkage. Allyl sulfides and trithiocarbonates cause bond rearrangement to reduce shrinkage. Functionalities that are capable of ACFT reaction like trithiocarbonates facilitate network rearrangement like thiol-enes and thio-urethanes. This leads to 25–54% of shrinkage stress reduction if they are added to dimethacrylates in the proportion of 1.5–2%. However, upon increasing their quantity to 30%, 65% of reduction in shrinkage stress can be achieved. While allyl sulfides in norborne-methacrylate monomers can reduce shrinkage stress from 35 to 95%.

Methylstyryl groups have been reported to have lower reactivity than methacrylate groups which causes delayed gelation resulting in stress relief. “phene” [N-methyl-bis(ethyl-carbamate-isopropyl-methylstyryl)amine] is an innovative monomer with high molecular weight. Further, it has lower double-bond concentration; the three properties together cause lower shrinkage, slow reactivity, and lower shrinkage stress. Phene (Fig. 22) is synthesized from N-methyl diethanol amine (MDEA) and 3-isopropenyl dimethylbenzyl isocyanate (IDI). Even at room temperature, methylstyrene groups have appreciable depolymerization. This causes slow polymerization rate and cross-linking density. Hence, Phene-containing composites have delayed vitrification and low polymerization shrinkage stresses. This is attributed to delocalization of double bonds owing to phene’s resonance structure. This inhibits the free-radical addition reaction and results in lower reactivity. In a study, up to 40% of Phene was added to conventional matrix and tested. It was found that the higher the Phene, the lower the shrinkage, shrinkage stress, flexural strength, flexural modulus, DC, and greater the wear and fracture toughness.

The lower molecular weight diluents have dense double bonds that increase shrinkage. They tend to increase mobility and decrease Tg. By just decreasing TEGDMA by half, shrinkage stress was found to decrease by 15–46%. Nevertheless, the stress values of low-viscosity low-stiff materials are equivalent to high-viscosity high-stiff materials. If polyethylene glycol (PEG) substitutes triethylene glycol (TEG), in the spacer, shrinkage can be reduced; however at the same time, Tg and mechanical properties will be decreased. Acetyloxypropylene dimethacrylate as a substitute for TEGDMA has been found to shrink less, however has less DC also. This is because the chain separating the unsaturation is comparatively shorter. Bis acryloxyethyltricyclododecan (TC-DI-HEA) has low viscosity and produced less shrinkage stress and hence can replace TEGDMA. As it has three aromatic rings in the backbone of the polymer, it has greater flexibility and can accommodate shrinkage better. Moreover, it has lower modulus and low-cross-linking potential which also aid in relieving stress. Commercially it is marketed as Venus Diamond.

The overriding factor on molecular mobility is the structure and functionalities of the monomers. For example, UDMA has two urethane groups with labile H atoms of NH groups. They favor chain transfer reactions like ~ M+ NH → ~ MH + N- where M- is a macroradical, while the NH group may be from monomer or polymer. So the NH is an active site and capable of reticulation which is the highest for UDMA among dimethacrylates. This results in a dense network. N- radical participates in cross-linking and hence the greater shrinkage of UDMA than BisGMA. If UDMA substitutes TEGDMA, shrinkage decreases to a great extent. However, if relative ratio of UDMA:BisGMA was increased, shrinkage increases.

Urethane dimethacrylate derivatives have been found to shrink less (Fig. 23). Low-shrinkage urethane dimethacrylate derived from isophorone (IP) disiocyanate, PEG in the presence of dibutylene diurate, and hydroxy ethyl methacrylate (HEMA) have been termed IP-UDMA (Fig. 24). They shrink less without compromising DC. Those derived from cycloaliphatic or aromatic disiocyanates (Fig. 23) shrank considerably less than fully aliphatic ones. Dimethacrylates with cyclohexyl methylenediisocyanate (CHMDI) or methylene diisocyanate (MDI) as core were found to shrink the least, nonetheless had lower hardness, Tg and modulus too.

Organogelators, like dibenzylidesorbitol (DBS) can induce physical gelation owing to their ability to form self-assembled networks. However, this reduces conversion. Less reactive solvents have been shown to reduce overall reaction kinetics and hence stress.

Polymerization inhibitors, like butylated hydroxy toluenes can be increased to extend pre-gelation stage and thus decrease shrinkage stress. However, the downside of this strategy is the reduced degree of conversion. Thus, this may not be a viable solution for decreasing shrinkage stress.

Certain commercial composites are formulated with less resin matrix volume to decrease shrinkage stress. One such material is Aelite LS, which has only 26% of resin matrix as opposed to 40% in other equivalent composites. Without any other modification, this method also proves to be useful in reducing both shrinkage and shrinkage stress.

Alternative Photoinitiators

A patent-registered UDMA molecule with an inbuilt photoinitiator (photomodulator) is being marketed as stress-decreasing resin (SDR). This has been found to have the least stress among many low-shrinkage materials including silorane. Its rigidity was also comparatively more. A randomized clinical trial of this resin for 3 years showed 0 failures as opposed to 1.3% of annual failure rate (AFR) for nanohybrids in posterior restorations. However, the difference was not statistically significant.
Just by reducing the content of camphorquinone, shrinkage and shrinkage stress can be reduced to 12% but it could also decrease degree of conversion.8

Copper(I)-catalyzed azide-alkyne cycloadditions (CuAACs)13,38 have been shown to have significantly less shrinkage and shrinkage stress than conventional photoinitiated polymerization.

Photoinitiated photo-CuAAC has certain advantages over camphorquinone (Fig. 25):
• Cu has longer lifetime and hence greater degree of polymerization and dark reaction.
• Step-growth nature of this causes narrow \( T_g \) and homogeneous networks.
• Delaying gelation means low stresses.
• The triazole in polymer enhances mechanical properties.

This click chemistry was introduced in 2001 as a robust and orthogonal alternative to conventional polymerization. CuAAC is prepared by mixing stoichiometric ratios of diazide and trialkyne (Fig. 26) with 2 mol% of CuCl\(_2\), N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA), CQ, and 4-ethyl dimethyl aminobenzoate (EDMAB). Such resins showed three to four times lower shrinkage stress than conventional resins. The gel point was delayed till 80% of DC occurred, while it happened at 5% of DC for conventional resins.38

1-Phenyl 1,2-propanedione (PPD) has been shown to produce less shrinkage stress by lowering the rate of polymerization.
Polymerization Shrinkage and Shrinkage Stress in Dental Composites

![Polymerization Shrinkage and Shrinkage Stress in Dental Composites](image)

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**Fig. 24:** Isophorone UDMA (IP-UDMA) *(Source: From Atai M, Ahmadi M, Babanzadeh S, et al. Synthesis, characterization, shrinkage and curing kinetics of a new low-shrinkage urethane dimethacrylate monomer for dental applications. Dent Mater 2007;23(8):1030–1041. DOI: 10.1016/j.dental.2007.03.004.)*

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**Fig. 25:** Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction *(Source: From Song HB, Sowan N, Shah PK, et al. Reduced shrinkage stress via photo-initiated copper(I)-catalyzed cycloaddition polymerizations of azide-alkyne resins. Dent Mater 2016;32(11):1332–1342. DOI: 10.1016/j.dental.2016.07.014.)*

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**Fig. 26:** Azide alkyne monomers, complimentary functionalized Si fillers and catalysts for CuAAC *(Source: From Song HB, Sowan N, Shah PK, et al. Reduced shrinkage stress via photo-initiated copper(I)-catalyzed cycloaddition polymerizations of azide-alkyne resins. Dent Mater 2016;32(11):1332–1342. DOI: 10.1016/j.dental.2016.07.014.)*

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Monoacylphosphene oxide (MAPO)-initiated composite exhibited low stresses (7 MPa) comparable to CQ (5.5 MPa) even at higher irradiance and very low stresses at normal irradiance unlike CQ-initiated ones. MAP0 delays the propagation stage of polymerization by diffusion-controlled mechanism. Also, it increases reaction temperature to increase molecular mobility and delays vitrification. However, in a systematic review on the role of photoinitiators and alternative initiators, it was found that they were the least effective in reducing shrinkage stress.
Alternative Coinitiators/Accelerators

Different tertiary amines (Fig. 27), such as 2-dimethylaminoethyl methacrylate (DMAEMA), N,N-cyanoethylmethylaniline (CEMA), N,N-dimethyl-p-toluidine (DMPT), N,N-diethanol-p-toluidine (DEPT), and N,N-dimethyl-p-aminobenzoic acid ethylester (DABE), can be used with the camphorquinone in the photoinitiation. Of these, DEPT produced the least shrinkage while DMAEMA the highest.

Bulk-fill Composites

These materials have modified initiators and fillers that enhance light transmission and hence reduce shrinkage stress. Under high compliance conditions, their low-viscosity versions worked as well as conventional packable composites. However, under low compliance, they reduce shrinkage stress greater than conventional low-viscosity materials. Hence, in a clinical situation, the cavity base which is a low-compliance area, bulk-fill low-viscosity composite can be used as a liner to reduce shrinkage stress.

In a systematic review cum meta-analyses, comparing bulk-fill and conventional composites to assess their clinical behavior and physical–chemical properties, 32 studies evaluated polymerization shrinkage, 20 shrinkage stress, 21 cuspal defection, 26 microhardness, 44 marginal quality, and 11 randomized controlled trials. They found that regular viscosity bulk-fill was similar to conventional, whereas flowable bulk-fill showed less shrinkage than flowable conventional. However, it was noticed that across the studies, 10 different methods were used to measure shrinkage. Cusp deflection of bulk-fill was lower than conventional. Marginal gap formation was similar in both the groups. Also, clinical performance at 10-year follow-up was similar. Only one study showed conventional to be better than bulk-fill at 6-year follow-up.

Ormocers

These are “organically modified ceramics” and hence the name. Their organic matrix has alkoxysilane that has $R_nSi(OR')_{4-n}$ where the central core Si–O is similar to ceramics and the R and R’ are multifunctional urethanes and thioethermethacrylates, respectively. They are essentially prepolymers with high molar mass and reduced double bonds in the R and R’ region that decrease shrinkage. They are claimed to have no residual unreacted monomers.

In a recently published meta-analyses on direct posterior composite restorations comparing low-shrink vs methacrylate-based composites, authors reviewed 21 clinical studies, of which 4 compared ormocer, 13 silorane, 3 bulk-fill, and 1 In Ten S with conventional methacrylates. They were found to be largely similar, except in one article on silorane; methacrylates had better marginal adaptation at 18-month follow-up. In general, at 12 months, methacrylates outperformed all low-shrink materials.

Conclusion

Clinically, polymerization shrinkage is assessed by measuring the marginal adaptation, marginal discoloration, secondary...
Polarization Shrinkage and Shrinkage Stress in Dental Composites

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