Management of Shrinkage Stresses in Direct Restorative Light-Cured Composites: A Review

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ABSTRACT

In spite of many advances in the field of dental resin composites, polymerization shrinkage continues to be a major problem. Shrinkage creates stresses within the material and its interface leading to marginal failure, staining, secondary caries, restoration displacement, tooth fracture, and postoperative sensitivity. The aim of this review is to explain the factors affecting shrinkage stresses, their consequences, and clinical strategies for their management.

CLINICAL SIGNIFICANCE

Polymerization shrinkage stress in dental composites is recognized as a significant material limitation that substantially complicates the placement of restorations. Shrinkage creates stresses within the material and its interface leading to marginal failure, staining, secondary caries, restoration displacement, tooth fracture, and postoperative sensitivity. This review explains the factors affecting shrinkage stresses, their consequences, and clinical strategies for their management. (I Esthet Restor Dent 25:305–316, 2013)

INTRODUCTION

Resin composites are widely used materials because of their bondability and aesthetic properties. They are finding increased application in modern preventive and restorative dentistry. A fundamental problem with the current dental resin composites based on dimethacrylates is dimensional shrinkage, an inherent manifestation in materials polymerizing through a free radical mechanism. Typical resin composites applied in restorative dentistry exhibit volumetric shrinkage values from less than 1% up to 6%, depending on the formulation and curing conditions.^{1,2}

This problem with dental restorative resins on adhesion is attributable to volume shrinkage arisen from an internal stress developed during polymerization. The internal contraction stress can damage the marginal seal of the bonded restorations. This may result in interfacial gap formation and produce postoperative sensitivity, marginal staining, or recurrent caries. Sometimes, cusp displacement may result in patient hypersensitivity or fracture and crack formation at surrounding walls.

The polymerization shrinkage stress is dependent on multiple factors. The material composition, polymerization reaction, degree of conversion (DC), boundary conditions, amount of material, and the resultant properties all play essential role in stress development and/or transmission to tooth structures.

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THE COMPOSITION OF THE RESIN COMPOSITE

The magnitude of stress is dependent on the material's volumetric shrinkage strain and its elastic modulus. The chemical composition of the resin matrix plays an important role over the magnitude, kinetics of shrinkage strain, and the elastic modulus development. A resin matrix formulated with monomers of high molecular weight (Mw) will result in lower shrinkage values than those formulated with monomers of low Mw. Thus, monomer functionalities, molecular structure, molecular mass, and size have major influences upon the amount of shrinkage and also monomer viscosity.^{3,4}

Examples of monomers used in dental composites include Bis-GMA, TEGDMA, UDMA, BisEMA. Bis-GMA has been widely used. It has high molecular weight (512 g/mol) and very high viscosity (500,000–800,000 mPa·s). Therefore, diluent monomers have to be used, or other ones have to substitute it, to make the resin more fluid. TEGDMA (mol. wt. 286 g/mol and viscosity 100 mPa·s) is an efficient diluents monomer. UDMA (mol. wt. 470 g/mol, viscosity 5000–10,000 mPa·s) can be used alone with TEGDMA or associated with Bis-GMA and/or some other monomers. There is wide range of other monomers that have been used and tested.

Particulate inorganic fillers are the stiff component in the resin composite. Several types, shapes, sizes, volume fractions and distributions of filler particles are used in commercial products. New options for reinforcing fillers generally have focused on nano-sized materials and hybrid organic–inorganic fillers. Organically modified ceramics were developed and have been used in commercial products.

The polymer matrix/filler ratio has a dominant effect upon strain and stress developed, and high values of shrinkage, combined with an increasing elastic modulus, produce increased stress within the composite structure and the bonding region.⁵ Filler surface area and the amount of the polymerizable coupling agent can contribute significantly to the shrinkage stress as well. The most commonly used coupling agent is γ -methacryloxypropyl trimethoxysilane. The polymerization process allows the methacrylate groups in the coupling agent to copolymerize with the resin monomers enhancing the interfacial adhesion.

The photoinitiator type and the photoinitiator/resin ratio directly affect the rate of polymerization and DC, so these two factors would also affect the rate and final magnitude of stress developed. Camphorquinone (CQ)/tertiary amine system has been recognized as a valuable visible light initiator since its invention in 1971. On the initiation mechanism, CQ (wavelength of maximum absorbance $[\lambda max]$: 468 nm) undergoes a so-called hydrogen abstraction type of photoinitiation mechanism in which CQ (a sensitizer) absorbs light to form a photoexcitation complex (CQ*-amine exciplex) with a tertiary amine (a hydrogen-donating agent) and subsequently generates amine-derived free radicals. Although CQ/tertiary amine system offers many advantages, the tertiary amine (π acceptor) can react with an acidic group, i.e., phosphoric acid, phosphonic acid, or carboxylic acid group (π donor) in adhesive monomers to form charge transfer complexes^{6,7} or undesirable quaternary ammonium salt.⁸ It was reported that the formation of quaternary ammonium salt resulted in increased time delay before light activation of the resin composite, hence ultimately resulting in degraded bond strength to dentin.³¹ All CQ/tertiary amine systems are not acid sensitive. It is highly dependent on the pKb of the amine. The most commonly used binary CQ-amine photoinitiator/ co-initiator system exhibits limitations for its use in dentin adhesive formulations. A certain level of phase separation has been suggested to exist due to the presence of water.9 Consequently, limited conversion from monomers into a rigid polymer network occurs when hydrophobic molecules are surrounded by a hydrophilic matrix. Some ionic derivatives of thioxanthone dyes are water miscible and represent an alternative for the polymerization of dental adhesives. In addition, iodonium salts are efficient water-soluble co-initiator system that improve the polymerization rate of dental monomers when CQ is used, even in the presence of a solvent.^{10,11} CQ can react with one or

more co-initiators to from free radicals in some cases, e.g., CQ + electron donor + electron acceptor such as a diaryl iodonium salt.

Unlike CQ/amine photoinitiator system, acylphosphine oxide and bisacylphosphine oxide do not require tertiary amines. These photoinitiators undergo an α -cleavage type of photoinitiation mechanism (Norrish type I system).

THE POLYMERIZATION PROCESS

Generally, the curing reaction in composite restorative materials involves visible-light-initiated photopolymerization of dimethacrylate monomers to form a highly cross-linked polymer. This photopolymerization reaction consists of three steps—initiation, propagation, and termination—and complexities arise in polymerization kinetics, network evolution, and the material property development^{12–15} With respect to the polymerization kinetics, both the propagation and termination reactions are diffusion controlled. Even at low conversion, the termination reaction, i.e., the coming together of two radicals that react to terminate each other, is diffusion controlled and slowed by the network.¹⁶ Subsequently, the radical concentration increases and the observed polymerization rate also increases, a phenomenon referred to as "autoacceleration." This process is important for dental composites since it results in rapid curing on clinically acceptable time scales.

In contrast to termination, the propagation reaction involves the reaction of a polymeric radical and a relatively mobile methacrylate moiety. This reaction's nature is such that it does not become diffusion controlled until significantly higher conversions, generally associated with the polymer becoming glassy, a process referred to as "vitrification." As the polymer vitrifies, the propagation reaction slows and the polymerization ceases, i.e., autodeceleration occurs. This process is particularly important in dental composites, where autodeceleration results in residual, unreacted methacrylates that remain in the composite restoration. In addition to complex polymerization kinetics, the polymer structure also evolves with numerous complexities. There are two critical, macroscopic demarcations that occur during polymerization. The first of these is the gel point conversion and represents the point at which an incipient gel is formed. In the chain-growth polymerization of dimethacrylates, this conversion is generally less than 5% to 10% and is critical for controlling the shrinkage stress.¹² The second macroscale demarcation is the vitrification point, which represents the conversion at which the polymer becomes glassy, accompanied by a dramatic modulus increase.

Direct placement restorations require that polymerization process be conducted at near ambient temperature, so photopolymerization is the preferred curing mode. Visible light activation over the range of 400 to 500 nm primarily based on the CQ/amine as the photoinitiator/co-initiator system remains the convention in dentistry. Blue light (400–550 nm) activates CQ and converts it to an excited triplet state. The excited CQ then reacts with a co-initiator to form free radicals, starting the polymerization process (activation and initiation stages).¹⁷ When this reactive radical reacts with a monomer molecule, an active center is created and propagates the process. The propagation reaction involves the polymer chain growth by rapid sequential addition of monomer to the active centers via covalent bonds until the maximum DC of C = C double-bonds into C-C bonds is achieved.

Before the polymerization process, Van der Wall forces act and keep the monomers grouped.

At this moment, the distance among the monomers is approximately 4 A°. During the polymerization process, these forces are substituted by covalent bonds, with distances of approximately 1.5 A°. Consequently, volumetric shrinkage occurs.^{4,5}

DEGREE OF CONVERSION

DC is defined as the degree (%) of conversion of polymerizable monomers to polymers. It is a very

important parameter used to measure polymerization performance. It is influenced by multiple factors: resin viscosity, the photopolymerization activity of photoinitiators and photosensitive resin monomers, and the wavelength, time, and intensity of irradiation lamps.

BOUNDARY CONDITIONS AND THE AMOUNT OF MATERIAL

In 1987, Feilzer et al.¹⁸ published a study showing that the expected magnitude of stress might be estimated through the ratio of the bonded to the unbonded areas, also known as the "configuration factor," or simply "C-factor." The higher amounts of bonded area result in higher stress level. On the opposite, a higher ratio of unbonded to bonded walls would be responsible for lower values of stress because shrinkage would freely occur at the unbonded surface areas. Although it is evident that the C-factor has important role in stress development, it has been suggested that the C-factor approach in isolation may overestimate the effect of the degree of constriction.¹⁹ In dental filling procedures, the cavity configuration varies according to the extent of caries removal, the amount of remaining healthy tissue, the tooth region and the tooth location (anterior, posterior), and type. Consequently, the level of stress might vary according to the clinical situation.

MATERIAL PROPERTIES

There are three inherent properties of the resin composites that are crucial over the magnitude of stress: the volumetric shrinkage, the material's stiffness (elastic modulus), and the degree of conversion from double carbon bonds into simple carbon bonds.

The complexity of polymerization shrinkage stress relies on the fact that these three components are interrelated and it is hard to identify the relative contribution of each individual factor; although some recent studies tried to isolate those. $^{\rm 20,21}$

ADHESIVE MONOMERS

An outstanding characteristic of adhesive monomers (adhesion-promoting monomers) is their ability to chemically interact with the tooth surface. On the molecular structure of adhesive monomers, it typically contains carboxylic acid group or its anhydride group, phosphoric acid group, or phosphonic acid group. Sulfur-containing adhesive monomers were developed for the purpose of adhesion to precious metals and their alloys.

Few of the commercially utilized carboxylic acid-type adhesive monomers, are NPG-GMA, PMDM, 4-META, 4- AETA, 4-MET, 4AET, MAC-10. Phosphoruscontaining adhesive monomers utilized in the formulations of commercial dental adhesives, are phenyl-P, 10-MDP, PENTA-P, and 6-MHPA. Phosphonic acid monomers, namely, MωP, EAEPA, and MAEPA were recently developed. In particular, to design single-bottle self-etching adhesives, they have received considerable recent attention because of their superior hydrolytic stability.^{22,23}

CLINICAL PROCEDURES TO REDUCE SHRINKAGE STRESS

The concurrent clinical and market trends such as desire to place of fewer increments, the development of lower shrinkage stress materials to address bulk curing, higher intensity light sources coupled with some claims of shorter cure time are the result of more recent research, and development efforts that have addressed the issue of polymerization shrinkage.

Many clinical methods have been proposed to reduce shrinkage stress, such as incremental layering techniques,^{24,25} control of curing light irradiance,^{26,27} and flowable resin liner application.²⁸ However, no method has been shown to be totally effective in abating the effects of polymerization shrinkage.

INCREMENTAL LAYERING TECHNIQUE

Many researchers have suggested the use of "incremental layering techniques" for resin-composite restoration to reduce the polymerization shrinkage stress and cusp deflection.^{24,25} The rationale is that shrinkage may be less detrimental when there are fewer bonded cavity walls involved at each stage of the restoration procedures. Incremental curing may enhance the degree of cure in thick sections and may undergo higher degree of cure due to lower light attenuation. It depends on many factors such as the optical properties of the material, light source intensity, and exposure time, etc. This yields better mechanical properties but higher shrinkage as well; however, the C-factor changes as well.

Nevertheless, the literature is not conclusive concerning the advantages promoted by the incremental layering technique over the effects of resin-composite polymerization shrinkage. Despite the controversy over the advantages of incremental build-up of resin composites, this technique has been broadly recommended in direct resin-composite restoration because it is expected to decrease the C-factor, allowing a certain amount of flow to partially dissipate the shrinkage stress.

LIGHT-CURING METHODS

Diverse photoactivation protocols have been advocated to reduce the polymerization stress.^{29,30} In theory, stress release by viscous flow before the vitrification stage would be allowed to occur without compromising the final polymer properties.³¹ Therefore, initial light exposure at lower irradiance values might lead to the formation of a reduced number of polymer growth centers, reducing the reaction rate and decreasing stress development due to the increased opportunity for resin flow before the vitrification stage.

There are many types of alternative light-curing methods. The "soft-start" protocol consists of initial light exposure with reduced irradiance for a certain period of time, followed by full irradiance. Another protocol is "pulse-delay" method, where the clinician may apply the initial exposure with reduced light irradiance for a very short period of time of a few seconds and follows a waiting period without irradiance (seconds or even minutes) and fully irradiate later.

The alternative light-curing protocols may not significantly affect final properties of the hardened material, some considerations should be noted: (1) the flowability of a material during an extended preset stage, may have minimal consequences because most shrinkage stress is developed during and after the vitrification stage.³² Therefore, opportunities for polymer relaxation would be restricted during the short period of light activation.³³ (2) Soft-start irradiation procedures give somewhat lower DC levels, associated with reduced stress.³⁴ (3) A reduced polymerization rate is associated with decreased cross-link density, manifested as a greater solvent-softening and/or lower final elastic modulus.³⁵

STRESS-ABSORBING LAYERS WITH LOW ELASTIC MODULUS LINERS

Flowable composites are low-viscosity resin-based restorative materials, which differ from conventional resin composites in their filler load and resin content. These materials are less rigid and could have a modulus of elasticity 20% to 30% lower than conventional hybrid composites. The use of a flowable resin composite as an intermediate thin layer has been suggested as a mean of overcoming polymerization shrinkage stress based on the concept of an "elastic cavity wall" suggested for filled adhesives.³⁶According to the "elastic cavity wall concept," the shrinkage stress generated by a subsequent layer of higher modulus resin composite can be absorbed by an elastic intermediary layer, thereby reducing the stress at the tooth-restoration interface manifested clinically as a reduction in cuspal deflection.37

However, actual implementation of such a "stress-absorbing" material is problematic. Flowable resin composites have shown shrinkage stress comparable to conventional resin composites, supporting the hypothesis that the use of flowable materials does not lead to marked stress reduction and the risk of debonding at the adhesive interface as a result of polymerization contraction is similar for both type of materials.³⁸

PREHEATING

Recently, preheating resin composites have been advocated as a method to increase composite flow, improve marginal adaptation, and monomer conversion. The benefits of preheating composites may have an impact on daily restorative procedures as well, with the application of shorter light exposure to provide conversion values similar to those seen in unheated conditions.³⁹ The reasons for increased conversion are based on many factors. Increased temperature decreases system viscosity and enhances radical mobility, resulting in additional polymerization and higher conversion.

CHANGES IN MATERIAL FORMULATIONS

Formulations containing one or more of the base monomers, BisGMA, EBPADMA, UDMA, and TEGDMA, have been utilized commercially for decades. A vast amount of research has focused on developing systems with alterations and improvements to the formulations, including the incorporation of monomethacrylate diluents, dimethacrylates, and multimethacrylates.

Multimethacrylates

Modifications of bisphenol-A-based dimethacrylate systems have included the use of pendant bulky (aromatic) constituents⁴⁰ as well as pendant alkyl urethanes⁴¹ to increase molecular weight and thereby decrease volume shrinkage. Derivatives of urethane dimethacrylate have been synthesized to increase molecular weight, reduce water sorption, and/or increase mechanical properties by incorporating aromatic or aliphatic groups. Bile acids were utilized as starting materials to form multimethacrylate monomers.⁴² These materials showed reduced volume shrinkage and promising mechanical properties; however, they exhibited extremely high viscosities (higher than BisGMA).

Monomethacrylate Diluents

These monomers contain secondary and tertiary functionalities that lead to their unique polymerization and polymer property behavior. These monomers exhibit rapid polymerizations that rival and often exceed those of equivalent di(meth)acrylates, and the polymers exhibit a high glass transition temperature. Additionally, the mono(meth)acrylates exhibit high conversion, limiting the potential for leachable monomer. These materials showed great promise when utilized as diluents, and several monomethacrylates were evaluated as alternatives to TEGDMA.^{43,44}

Acidic Monomers

Incorporating acidic monomers in relatively small mole fractions into methacrylate resins may enable a separate adhesive layer to be eliminated and result in improved overall performance. Acidic monomers have been synthesized from o-hydroxyaryl phosphonates that exhibited rapid polymerization kinetics.⁴⁵

Monomers with increased molecular weight such as Modified UDM Resin DX511 (895 g/mol), dimer acid monomer (673–849 g/mol) have been developed for composites with reduced shrinkage.⁴⁶ Urethane monomer TCD-DI-HEA has been shown to produce lower polymerization contraction stress.⁴⁷

NOVEL POLYMERIZATION MECHANISMS

Presently, composite restoratives suffer from several drawbacks associated with the chain growth nature of the methacrylate-based free radical polymerization process. It is fundamentally limited in several aspects. The chain-growth polymerization mechanism leads to early gelation,¹² whereas the methacrylate consumption is linked to a defined volume reduction associated with the consumption of each methacrylate.⁴⁸ Improvements

in the methacrylate monomer structure, as noted previously, have the potential for addressing many of the shortcomings of current composites; however, an even greater potential lies in completely changing the reaction mechanism, either by changing the active center (from radical to cationic), by changing the nature of the network/molecular weight evolution (by changing to a step growth reaction or by changing to a covalent adaptable network), by changing the nature of the reactive chemistry (by going to ring opening species), or by changing the physical behavior that arises during polymerization (by inducing phase separation).

Thiol-ene-based resins polymerize by a step growth radical polymerization mechanism. This result in reduced volume shrinkage per double bond and a delayed gel point conversion. The combination of reduced shrinkage and delayed gelation promotes significant reductions in shrinkage stress. However, they exhibit reduced mechanical properties relative to dimethacrylate-based systems.^{49,50} The use of thiol-enes as reactive diluents in ternary formulations results in a synergistic combination of both thiol-ene polymerization kinetics and shrinkage dynamics with dimethacrylate mechanical properties.⁵⁰ The hybrid nature of methacrylate-thiol-ene polymerization results in even greater reductions in shrinkage stress without compromising mechanical properties.

Silorane resin reveals lower polymerization shrinkage compared to the dimethacrylates. These "cyclic" monomers "open" their molecular structures with local volumetric expansion and this may partly or totally compensate for volumetric shrinkage from C = C or similar polymerization.^{51,52}

Besides change in the resin matrix composition, studies have demonstrated reduced shrinkage stress through alterations in filler content. Condon and Ferracane⁵³ suggested that addition of nonbonded 40-nm colloidal silica might act as stress-relieving sites through plastic deformation. They also verified that composites with nanofiller particles treated with a nonfunctional silane developed 50% less stress than composites fully treated with the functional coupling agent. Efforts to modify fillers have been aimed at improving the properties of composites by the addition of polymer nanofibers, glass fibers, and titania nanoparticles.^{54,55} Silsesquioxane nanocomposites, which are essentially an organic–inorganic hybrid molecule, reduce shrinkage, but also reduce mechanical properties if used in too high of a concentration.⁵⁶ Changes in the photoinitiator systems and polymerization inhibitors have also been reported. Another possible approach is inclusion of a component readily allowing plastic deformation during stress development, such as ultrahigh molecular weight polyethylene fibers.⁵⁷

Thus, many factors affect the polymerization efficiency, be they intrinsic; photoinitiator type and concentration, viscosity (co-monomer composition and ratio, filler content) and optical properties, or extrinsic; light type and spectrum, irradiation parameters (radiant energy, time, and irradiance), curing modes, temperature, and light guide tip positioning.⁵⁸

CONCLUSION

The success and longevity of the dimethacrylate-based dental resin composites restoration can be compromised because of their inherent association with dimensional shrinkage. Various clinical procedures have been proposed to reduce shrinkage stress, but none of the methods has shown to be totally effective in abating the effects of polymerization shrinkage. The field of composite dental restoratives continues to propose and achieve significant and exciting advances in resin formulation, filler loading and modification, and curing methodologies and mechanisms.

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