Factors involved in the development of polymerization shrinkage stress in resin-composites: A systematic review

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Summary *Objectives*. Polymerization shrinkage stress of resin-composite materials may have a negative impact on the clinical performance of bonded restorations. The purpose of this systematic review is to discuss the primary factors involved with polymerization shrinkage stress development.
Data. According to the current literature, polymerization stress of resin composites is determined by their volumetric shrinkage, viscoelastic behavior and by restrictions imposed to polymerization shrinkage. Therefore, the material's composition, its degree of conversion and reaction kinetics become aspects of interest, together with the confinement and compliance of the cavity preparation.
Sources. Information provided in this review was based on original scientific research published in Dental, Chemistry and Biomaterials journals. Textbooks on Chemistry and Dental Materials were also referenced for basic concepts.
Conclusions. Shrinkage stress development must be considered a multi-factorial phenomenon. Therefore, accessing the specific contribution of volumetric shrinkage, viscoelastic behavior, reaction kinetics and local conditions on stress magnitude seems impractical. Some of the restorative techniques aiming at stress reduction have limited applicability, because their efficiency varies depending upon the materials employed. Due to an intense research activity over the years, the understanding of this matter has increased remarkably, leading to the development of new restorative techniques and materials that may help minimize this problem.
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Introduction

In the last three decades, adhesive dentistry has evolved remarkably, greatly due to the development, in the late 1950s, of BisGMA-based composites [1]. The incorporation of new monomers (e.g. UEDMA, BisEMA), new initiation systems and filler technologies have significantly improved the physical properties of these materials, expanding their use as direct and indirect restoratives. However, even considering the intense research on bonding mechanisms between composites and the dental substrate, clinical failure due to the disruption of the bonded interface remains a frequent occurrence [2]. Such interfacial defects may develop as a consequence of long-term thermal and mechanical stresses, or during the restorative procedure itself, due to stresses generated by composite polymerization shrinkage [3]. In fact, a direct relationship between polymerization shrinkage stress and marginal integrity has been demonstrated, in vitro, in class V restorations [4–6] and in teeth restored with bonded porcelain inlays [7].

Contraction stress in composite restorations is the result of polymerization shrinkage taking place under confinement, due to bonding to cavity walls. The material's viscoelastic behavior, characterized by its flow capacity at early stages of the curing reaction and by the elastic modulus acquired during polymerization, has also been identified as another important factor in contraction stress development [8].

As both volumetric shrinkage and viscoelastic properties are influenced by the same variables, accessing their specific role on stress development is a difficult task. For example, composites with relatively high inorganic filler content present lower shrinkage values but higher stiffness (i.e. lower strain capacity), compared to materials with lower inorganic content [9,10]. On the other hand, increasing degree of conversion of the polymer matrix increases volumetric shrinkage and elastic modulus simultaneously [11,12]. The complexity of this issue is heightened by the fact that stress development is affected by reaction kinetics. As the composite's plastic deformation (or viscous flow) is a time-dependent event, slower curing rates may provide extended periods where the material is able to yield to contraction forces before acquiring higher elastic modulus [13]. In fact, reducing polymerization rates in composites has been shown to lower stress levels significantly [14–16].

The influence of confinement conditions imposed on the composite sample and the compliance of the bonding substrate have also been a subject of intense debate in the literature. A direct relationship between contraction stress and confinement of the composite sample was found when a rigid, non-compliant testing system was employed [17]. However, other authors have found that these two variables were inversely related when using a less rigid, more compliant set-up [18,19].

From a clinical standpoint, it is important to determine how these laboratory results can be applied to the restorative procedure. The purpose of this systematic review is to discuss the various factors that influence the development of contraction stresses in dental composites, i.e. volumetric shrinkage, viscoelastic properties, and extent of cavity constraint, as well as their influence on different aspects of the restorative procedure.

Volumetric shrinkage

When monomers in proximity react to establish a covalent bond, the distance between the two groups of atoms is reduced and there is a reduction in free volume, both of which translate into volumetric shrinkage. The magnitude of volumetric shrinkage experienced by a composite is determined by its filler volume fraction and the composition and degree of conversion of the resin matrix.

Shrinkage values reported for BisGMA (5.2%) and TEGDMA (12.5%) are substantially higher than those displayed by typical composites, which range between 2 and 3% [9,20,21]. This difference is due to the fact that in hybrid composites, approximately 60% of the volume is occupied by filler particles. Microfilled composites, though their inorganic content is typically about 40 vol%, have shrinkage values similar to hybrids, due to the presence of pre-polymerized composite particles, sometimes referred to as 'organic fillers', which render them similar to hybrid composites in terms of the actual volume fraction of polymerizing resin. Low-viscosity (flowable) composites present volumetric shrinkages up to 5%, in large part due to their reduced inorganic content, which is typically below 50 vol% [9]. The shrinkage values reported should be considered approximate, because they are completely dependent upon the extent of the polymerization reaction. This makes the comparison of shrinkage data from different studies a tenuous proposition, as it is not typical for authors to measure degree of conversion along with shrinkage, except in rare cases [15,16].

The volumetric shrinkage of composites has been shown to be proportional to its degree of conversion

[12,16]. In the photoactivated materials, degree of conversion is determined by the product of light irradiance and exposure time (radiant exposure, J/cm^2) [22]. As curing rate is proportional to the square root of the light intensity applied to the composite [23], it has been proposed that the method by which light energy is delivered to the composite is capable of delaying the acquisition of elastic modulus, allowing polymeric chains to re-arrange and microscopically and macroscopically accommodate the reduction in volume by plastic deformation [24]. It is the so-called 'rigid contraction' (sometimes previously referred to as 'post-gel contraction') that is the fraction of the total volumetric shrinkage responsible for stress development [25,26]. In the photoactivated composites, the fast reaction rate virtually eliminates the time allowed for viscous flow, and it is estimated that the polymer matrix becomes 'rigid' within seconds after a relatively low degree of conversion [27]. As a result, stress begins to build-up almost immediately after polymerization is triggered [6], and nearly all of the shrinkage occurs after the polymer matrix has reached a significant level of rigidity, the magnitude of which continues to increase with time. Self-cured composites, on the other hand, develop lower contraction stress values than light-cured materials, in part due to their slower reaction rate, but also because the self-initiated reaction generates a smaller number of free-radicals than photoactivation, often resulting in lower degrees of conversion [7,13].

In order to reduce polymerization rate and extend the time allowed for viscous flow (and, consequently, for non-rigid shrinkage) several photoactivation methods have been proposed as alternatives for continuous high-intensity irradiation [28,29]. These curing routines, generically referred to as 'soft start', use reduced light irradiance during the first few seconds of light activation, switching to high irradiance for the remaining curing time in order to provide the material with sufficient radiant exposure. The efficacy of these curing methods has been demonstrated by several studies reporting significant reductions in shrinkage strain when compared to continuous high-intensity photoactivation [12,22,30,31]. However, significant reductions in reaction rate do not necessarily correspond to significant reductions in contraction stress [14,16]. One hypothesis that might explain this discrepancy is the above-mentioned fact that dimethacrylate composites develop elastic modulus at very low conversions [27]. Therefore, even at relatively low reaction rates, the stage in the conversion where the composite ceases to allow significant plastic

deformation is reached rapidly. Therefore, it is likely that only impractical applications of low light power for prolonged periods may provide the slow reaction rates necessary to significantly reduce composites contraction stresses in the clinical situation.

Reducing contraction stress by changing polymerization rate has limitations. First, its efficacy varies according to composite formulation. A study evaluating the effect of low curing rates on contraction stress development of three commercial materials found stress reductions between 19 and 30% [15]. A photoelastic study observed stress reductions between 3 and 7% in five composites [32]. Another potential problem with this method is that it may produce alterations in the nature of the polymer network formed. Some studies have provided evidence that suggests that the quality of the polymer network formed is independent of the mode of light energy application, and is solely dependent upon the overall degree of conversion [33,34]. However, other researchers have observed that materials cured by non-continuous photoactivation were more susceptible to ethanol degradation than those photoactivated using continuous high-intensity irradiation, even though their degrees of conversion were equivalent [35–37]. The authors have suggested that the use of low irradiances generates a small number of free radicals, resulting in longer polymeric chains with low cross-linking density, evidenced by a more severe softening effect of the ethanol. Unpublished observations suggest that this negative effect may not be the result of low initial irradiances per se, but the association of slow curing with a relatively low overall energy application.

The concentration of diluent in the resin matrix also affects shrinkage. A recent study verified that higher TEGDMA/BisGMA ratios in experimental composites resulted in higher contraction stress values due to increased volumetric shrinkage, as a result of enhanced conversion [38]. Because they typically have lower molecular weight than the host monomers, 'diluent' monomers increase the density of polymerizable carbon double bonds, which may lead to more shrinkage. Furthermore, the mobility in the reaction environment is increased due to the lower viscosity and T_g of the diluent, allowing a more efficient conversion [39]. It is interesting to note that the reduction in composite viscosity and stiffness resulting from high diluent concentrations was not able to compensate the effect of increased shrinkage on stress development [40]. This result suggests that conversion and its resultant volumetric shrinkage are the most

important factors affecting the development of contraction stress in dental composites.

Several studies have found that for regular or packable composites, contraction stress is directly proportional to filler content, regardless of differences in matrix composition [6,41,42]. Those findings suggest that within a relatively narrow range of shrinkage values, viscoelastic characteristics are determinant factors in stress development. However, stress values produced by composites having lower filler content to produce lower viscosity, and consequently lower stiffness, are similar to those displayed by other materials possessing higher filler contents and greater stiffness [43]. This indicates that when a wide range of shrinkage values is considered, volumetric shrinkage prevails over viscoelastic properties in determining contraction stress.

Viscoelastic behavior

Resin composites are solids with complex viscoelastic behavior. When submitted to an instantaneous load that generates stress below the elastic limit, these materials undergo elastic deformation which is promptly recovered at load removal. If the load is applied for a certain length of time, these materials begin to present viscoelastic deformation, characterized by a combination of elastic deformation that is recovered after load removal and viscous (permanent) deformation. The response to load application is dependent on the composite's filler content [44], matrix chemistry, and degree of conversion [39]. Strain capacity is inversely related to inorganic filler content [10]. Considering the relatively narrow range of volumetric shrinkage values displayed by hybrids and microfilled composites with regular consistency, contraction stress onset and its final value are directly affected by the composite's inorganic content [6,42]. Microfilled composites usually develop lower stress values compared to hybrids due to their lower elastic modulus, higher strain capacity and similar volumetric shrinkage [9]. Likewise, materials with high degrees of conversion undergo less deformation, because enhanced polymer chain entanglement and high cross-linking density hinders chain movement in the polymer network [11].

Initially, some studies tried to characterize contraction stress development using the linear elastic model [24,26]. According to this model, the increment in stress for a certain time interval would be proportional to the product of the increase in volumetric shrinkage by the increment in the material's elastic modulus, according to Hooke's law. However, the stress values calculated by this method were far greater than those verified in mechanical tests [4]. The difference between calculated and observed stress is explained by the occurrence of viscous flow, mostly occurring prior to the acquisition of significant elastic modulus.

Early in the polymerization reaction, composites present a predominantly viscous behavior and, gradually, they become predominantly elastic [10]. The idea that viscous flow accommodates a significant fraction of the total volumetric shrinkage is supported by studies that measured contraction stress development as a function of degree of conversion. These studies agree that stress build-up occurs at a faster rate at high conversions [16,45]. A possible hypothesis to explain such findings is that early in the reaction, chain growth and primary cyclization occur preferentially to cross-linking. The absence of covalent bonds between polymer chains would allow plastic deformation and stress development would be relatively slow. Beyond a certain conversion level, cross-linking would prevail, and small increments in conversion would lead to significant increase in stress, due to the high stiffness of the polymer network. This rationale is supported by studies showing that the glass transition temperature of composites, considered an indicative of cross-linking density, also increases at a faster rate at high conversion levels [27,46].

Nevertheless, even after acquiring measurable elastic properties, the composite material is able to flow [38]. Two studies evaluated contraction stress in relation to shrinkage strain development. One study found that a self-cured composite had developed less than 10% of its maximum stress when shrinkage strain had reached 50% of its final value [47]. In the second study, there was a two-second delay between detectable shrinkage strain and contraction stress offset in a photoactivated composite [40].

As mentioned before, changes in composite structure during the early stages of conversion are characterized mechanically by an increase in viscosity and elastic modulus. The ratio between these two parameters is denoted by the 'stress relaxation time', and represents the time necessary for the stress to decline to $1/e$ ($\sim 37\%$) of the initial value [48]. As viscosity is a time-dependent property, the material should present relatively low viscosity in order to be able to yield to contraction forces and postpone stress build-up. After the material begins to acquire elastic modulus, a low stress relaxation time is preferable to allow for more rapid plastic deformation to

relieve stresses. Therefore, the influence of reaction kinetics on stress development becomes evident. Fast curing rates do not allow enough time for viscous flow. Moreover, elastic modulus acquisition in composites occurs rapidly [49], which further shortens the time available for stress relaxation. Thus, rate of conversion is a significant factor affecting the generation of contraction stress in dental composites, though it is not possible to determine the magnitude to which it influences stress in relation to the other significant factors like volumetric shrinkage and elastic modulus, because they are all interrelated.

Restrictions imposed on composite shrinkage

When composite shrinkage is restricted by adhesion to the cavity walls, two variables must be considered. First, the level of confinement imposed on the material, which is estimated as the percentage of composite surface that is bonded to the substrate in relation to the total surface area, and second, the compliance of the bonding substrate. The substrate's compliance, is characterized by the stiffness and mobility of its walls. For example, the compliance of a mesio-occlusal-distal preparation is related to the elasticity of the dentin and enamel substrate and to the possibility of cuspal deflection. The effect of confinement and compliance of the bonding substrate on stress values and on the integrity of the bonded interface has been the object of intense debate in the literature.

The majority of the information regarding contraction stress development has been obtained through mechanical testing. The most frequently used set-up consists of placing the composite between two flat surfaces (usually metal or glass) connected to the opposing fixtures within a universal testing machine. In order to create a highly rigid (i.e. near-zero compliance) confinement condition for the curing composite, the approximation of the opposite bonding substrates due to the material's axial shrinkage is constantly monitored by a feedback system and counteracted by the displacement of the cross-head in the opposite direction, keeping the specimen height constant [3,17,42]. Therefore, the load cell registers the force necessary to keep the initial height of the specimen, and stress is calculated by dividing the force by the cross-section area of the bonding substrate. Some authors choose not use a feedback system to keep the specimen height constant

[18,19,41]. In this case, the composite is able to shrink in its long axis without restriction, other than that represented by the force needed to deform the load cell and other components of the testing apparatus that may resist the shrinkage. Recently, a novel stress measuring device based on the cantilever beam theory has been introduced, with the main feature of allowing variations in the system compliance, in order to mimic the compliance o the tooth structure [50].

As with any method, contraction stress measurements via mechanical testing present limitations. The main drawback refers to the fact that, though the shrinking composite develops a tri-axial stress state, only the stress manifested in the long axis of the specimen is registered [51]. Another criticism refers to the low compliance of the testing system, resulting from the high stiffness of the material used as bonding substrate, associated with the axial restriction to shrinkage. It is reasonable to assume that the deformation of the dental substrates would relieve part of the stress during the curing of composite restorations [50]. Consequently, a near-zero compliance testing set-up would overestimate stress values, which may range from 4 to 25 MPa, depending on the composite tested, specimen dimensions and photoactivation method [15,42, 52]. However, a photoelastic study found that, considering an ideal adhesion of the composite to the cavity walls, contraction stress can reach up to 23 MPa at the internal angles of the cavity [53], which leaves this question open. In spite of the controversy, studies have demonstrated a good correlation between stress values obtained using low compliance systems and results of microleakage in bulk-filled composite restorations [5,6].

In order to describe confinement conditions and correlate them with stress values, the term 'cavity configuration factor' (C-factor) was created, and is defined as the ratio between bonded and unbonded surfaces of the composite specimen [17]. Using a near-zero compliance testing system, the authors observed that higher C-factors corresponded to higher stress values. Since composite flow is more likely to occur from the free surfaces of the specimen, a higher proportion of free composite surface would represent a smaller restriction to shrinkage, thereby reducing stress. In contrast, when free surface is reduced, shrinkage perpendicular to the long axis of the specimen is restricted by the adhesion to the substrate and a larger proportion of the volumetric shrinkage manifests in the long axis of the specimen, increasing stress values [51,54]. The influence of the confinement on stress values was confirmed in previous studies using a similar testing apparatus [24,52]. However,

when composite shrinkage on the long axis of the specimen is only partially restricted, C-factor and stress seem to be inversely related [18,55]. Moreover, the volume of shrinking composite becomes a variable to be considered. For a certain bonded area, taller specimens, which would have lower the C-factor, exert higher contraction forces on the load cell of the testing machine [19].

The application of the C-factor concept to clinical practice must be done very carefully. Cavity preparations present a much more complex geometry than the specimens used in in vitro mechanical testing, resulting in a very heterogeneous stress distribution [51,53]. Photoelastic and microleakage studies suggest that the C-factor would be applicable to restorations only when comparing cavities with similar volume [56,57]. In restorations with different volumes, minimal correlation was found between interfacial gaps and C-factor [58].

The use of incremental insertion techniques for the purpose of reducing the effects of cavity confinement has also been questioned by some authors. Finite element analysis, photoelastic and microleakage studies have found no significant reduction in stress or enhancements in marginal adaptation when composite is inserted in small increments compared to insertion in bulk [59-61]. These findings suggests that either the confinement is not a determinant factor in stress development of dental restorations in natural teeth, or that the reduction in C-factor obtained by incremental insertion is not sufficient to cause significant stress reduction.

Clinically, stress magnitude can be reduced by applying a low stiffness material between the composite restorative and the cavity walls to increase the compliance of the bonding substrate. Another benefit from this procedure is that stress distribution is more uniform along the low elastic modulus layer [62]. This technique, known as 'elastic cavity wall' is accomplished with the use of an intermediate layer of low-viscosity composite between the adhesive layer and the restorative composite [63]. In vitro evaluations of this technique, however, show inconsistent results [64,65].

Two factors interact to produce significant stress relief with the use of a low-stiffness layer: the thickness of the intermediate layer and its elastic modulus [66]. Thicker layers favor stress relief because elongation, in absolute numbers, is proportional to the material's initial dimension [67]. A study using finite element analysis verified a reduction of 10% in shear stresses at the tooth/restoration interface in a situation where a 40-μm layer of intermediate material with elastic modulus of 5 GPa was included in the model, compared to the control condition (without intermediate layer). When the thickness was increased to 80 μm, stress reduction was 38% [68]. Other authors found that an increase from 40 to 200 μm in the unfilled resin layer thickness applied to the bonding substrate of a mechanical testing set-up resulted in a 24 and 30% reduction of the stress developed by a hybrid composite, depending on the C-factor of the composite sample [4]. In the same study, the application of thicker layers of unfilled resin to cavity walls of cylindrical class V restorations resulted in significant reduction in leakage.

Besides differences in thickness, discrepancies among authors may happen due to differences in the elastic modulus of the materials used as intermediate layers. Elastic modulus of low-viscosity composites varies greatly, with values between 6.5 and 12.5 GPa being reported [9]. A previous study compared five low-viscosity materials (with flexural modulii between 4.1 and 8.2 GPa), one unfilled resin (2.1 GPa) and a regular-viscosity composite (12.3 GPa) as pre-cured substrate for a hybrid composite. Observed stress reductions were between 22 and 53%, but these were only significant with the unfilled resin and one of the flowable composites [43]. Interestingly, the composite allowing significant stress reduction was not the least rigid, suggesting an inconsistent behavior of low-viscosity composites with flexural modulus in the range of 4 and 6 GPa as intermediate materials. Also, these results suggest that some low-viscosity composites would not be indicated to increase the compliance of the cavity walls and reduce stress build-up.

Composite flow may also be increased by modifications in material's structure. Though the alternatives described below are experimental, some of them may serve as the basis for future material development. The incorporation of pores in unfilled resin was shown to reduce stress between 17 and 42% [69]. The authors suggested that the presence of pores increase the material's free surface, facilitating flow. Also, the oxygen in the pores may reduce degree of conversion, which also contributes to reducing the stress. However, this is an option of limited applicability, as a porous material may have its cohesive strength impaired. Unbonded filler particles were also tried as a way to increase the available sites for composite flow, without reducing its mechanical properties [70]. Stress reduction observed in hybrid and microfilled composites ranged between 30 and 50%, respectively. Subsequent studies have shown that the use of unbonded nanofiller did not significantly reduce flexural strength or fracture toughness of composites materials [71]. In vivo, however, a tendency

for increased wear after 1 year was observed [72]. High-density polyethylene (HDPE) spheres were also tried as additives or substitutes of part of the inorganic filler [73]. When 20 wt% of HDPE was use, stress reductions up to 25% were accomplished either by reduction in volumetric shrinkage (when added to the microfilled composite) or by reduction in elastic modulus (when replacing part of the filler in the hybrid composite). However, the applicability of this approach in hybrid composites is limited by the significant reduction in mechanical properties observed.

Conclusions

An intense research activity in the last few years brought many contributions to the knowledge on polymerization contraction stress of resin composites. Nevertheless, several aspects regarding this extremely complex phenomenon remain unclear. Considering the inherent volumetric shrinkage of BisGMA-based materials and the desire to maximize degree of conversion and elastic modulus for enhanced clinical performance, maximizing viscous flow seems to be a key mechanism to reduce stress. Therefore, further investigations on viscoelastic behavior and reaction kinetics of these materials are necessary. The resources currently available to reduce contraction stress are somewhat limited. Nevertheless, based on scientific evidence, a few aspects of clinical interest can be observed:

1. Volumetric shrinkage should not be the only parameter considered to predict composite behavior regarding stress development. Materials with relatively low shrinkage due to high inorganic filler content also present high elastic modulus, which may result in increased stress.
2. Reduced polymerization rate due to the use of alternative photoactivation methods does not necessarily lead to significant reductions in contraction stress. Also, a particular curing routine may not be efficient with composites from different manufacturers. Stress reduction cannot be achieved at the expense of adequate degree of conversion.
3. Increasing the compliance of the cavity walls by applying an intermediate low-modulus layer may lead to significant stress relief depending on its thickness and elastic modulus. Some low-viscosity 'flowable' composites may be too stiff to be successfully used for this purpose.

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