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Polymerization shrinkage in contemporary resin-based dental composites: A Review Article

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Abstract

Polymerization shrinkage of the resin-based dental composite restorations has crucial implications on the clinical performance and durability of the resin composite restoration. Polymerization shrinkage is an inherent property of the photo-cured methacrylate composite Thus, contemporary resin-based dental composites try to achieve novel chemistry in a commercial resin composite to limit the polymerization shrinkage to minimum by alteration of resin part and addition of inorganic fillers

Keywords: Resin composite; Polymer; Polymerization shrinkage; Matrix; Fillers;; Dental restorations; Polymerization.

1. Introduction

Resin-based direct dental composites are the most popular polymeric materials used for restoration of teeth[1]. Even though the chemical improvement in resins production of photocured resin-based dental composites to avoid their inherent problem of polymerization shrinkage. polymerization shrinkage is persisting. However, Indirect resin composites could be used alternatively to direct dental composites to decrease the polymerization shrinkage, direct dental resin composites are more satisfactory, as they do not need the use of a dental laboratory steps and done completely inside the mouth with little time and equipment[2]. A great concern has been made to decrease the effects of polymerization shrinkage to minimum. Current review includes the contemporary improvement of the chemical composition of the resin-based direct dental composites.

Methyl methacrylate resin-based dental composites are mostly cured via photo-cured light curing system using blue-light at a wavelength ranging between 420-480 nm. During these process, double carbon bonds (C=C) in the monomer are changed to single bonds (C-C) in the formed polymer. The degree of conversion (DOC) is the number molecules changed to polymer. Both mechanical and physical feature of resin-based dental composites are influenced by the extent of DOC

during polymerization reaction. The higher the DOC, the higher the performance and longevity of the resin-based dental composite restorations[3].

Most of resin-based dental composites showed considerable amount of residual monomers in the cured resin, which could attributed to the effects of many contributing factors as; irradiation time and distance, type of light source, wavelength, power density and type of monomers and inorganic fillers in addition to type and quantity of photo-initiators[4].

The process of polymerization comprises a certain degree polymerization shrinkage (PS) which occurred mainly due to the chemical contraction of the formed polymer. This chemical contraction occurred due to reduction in the distance between the atoms of monomers, which lead to bulk contraction in polymerized resin which is referred as volumetric polymerization shrinkage. The volumetric polymerization shrinkage of resin-based dental composites is generally ranging between 1–6%[5,6].

The polymerization shrinkage tends to develop a stress at the tooth/restoration interface which is termed polymerization stress. Zero polymerization shrinkage is one of the ultimate goals of the restorative dentistry to avoid accumulation of the stresses. These stresses eventually create marginal gap and micro-infiltrations with ingestion of food debris and bacteria at

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tooth/restoration interface, which is referred to marginal leakage[7]. The end results are impairment the esthetics appearance of dental composite restorations and subsequent of major problems such as teeth sensitivity, recurrent dental caries and fracture of tooth and or restoration[7–11]. Figure 1 represent a diagrammatic illustration of the polymerization shrinkage direction developed at tooth/restoration interface. Figure 2 display scanning electron microscope image showing polymerization shrinkage and marginal gap formation in conventional methacrylate-based resin composite restoration. Table 1 summarized he basic requirements of the monomers to be used in the resinous phase of dental composites[12].
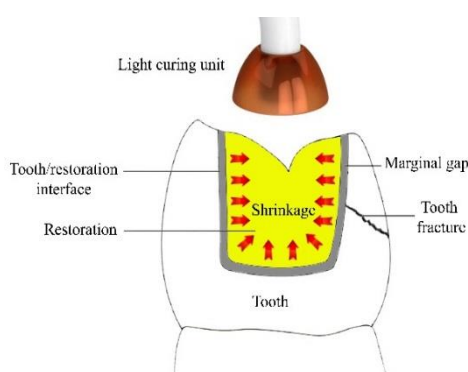

Fig. 1. A diagrammatic illustration of the polymerization shrinkage direction developed at tooth/restoration interface.
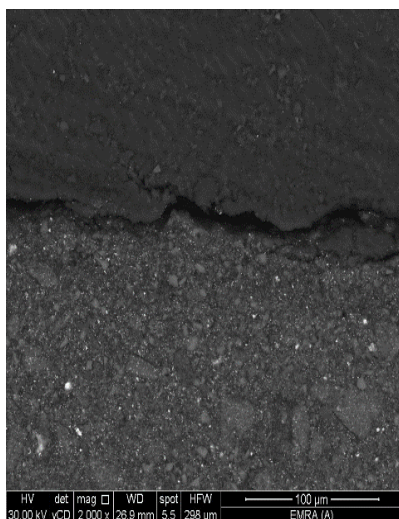

Fig. 2. Scanning electron microscope image showing marginal gap formation due to polymerization shrinkage of conventional dental composite.

Table 1:Basic requirements and functions of the monomer to be used in resin matrix of dental composites.

Basic requirement	Function
Crosslinking agent	Adequate mechanical properties
Low polymerization shrinkage	To avoid marginal gap
High polymerization rate	Low curing time
Minimum water uptake	To increase the durability
High color stability	Long-term aesthetics

Photochemical polymerizationt:

Photopolymerized (photo-cured) dental resin composites basically utilizes photons to initiate the polymerization procedure via photochemical oxidation of the monomer in the presence of photo-curing source[7].

Polymerization shrinkage:

During the process of polymerization, the weak physical van der waals attraction between the monomer molecules are replaced by a stronger covalent bond and thus development of shrinkage[13]. Polymerization shrinkage in the contemporary resin-based dental composites is challenged to be compensated and or diminished by using a variety of methods depends on novel chemistry in a commercial resin composite by modifications of resin matrix and or fillers content of the polymer[10,14].

Polymerization mechanism:

Polymerization mechanism could be categorized into addition and condensation polymerization. In mechanism of addition polymerization, the chain grows without by-product formation. It can be classified into free radical (as in Bis-GMA dental composites) and ring-opening reactions (as in silorane-based resin). While, in the condensation polymerization, elimination of a small molecule occurs upon reaction producing a larger one without involvement of free radicals. Water is mainly formed during the chain growth as a by-product[15].

Free Radical Polymerization:

This mechanism is referred alternatively as addition polymerization because molecules are added to the polymer during propagation. Methacrylates- based dental resin composites are polymerized by this type of polymerization rection. It includes three stages which are; activation, initiation which requires activation by external source as light to produce a free

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radical which attacks the functional or reactive group (carbon double bond) in the monomer, resulting in the formation of a carbon single bond and an unpaired electron. The reaction proceed and propagation take place. The chain growth continued till no free radicals are combined to it, resulting in the polymerization termination[15].

Ring-opening Polymerization

The cationic reaction began with the initiation stage of the acidic cation, where the oxirane ring is opened and produces a new acidic center. Addition of oxirane monomer. The epoxy ring is then opened forming a chain, thus formation of polymer network[15].

Chemistry and compositions:

Resin based dental composites are essentially consists of three distinct phases: high strength inorganic dispersed phase (filler), low strength organic matrix phase, and an interfacial phase (organosilane or coupling agent) for intimate bonding of both fillers and organic matrix[16].

Reinforcing Phase

Inorganic fillers are added to the resin matrix to induce many benefits such as; reinforcement of the resin composite[17], aesthetic demands[18], and to decrease the polymerization shrinkage by reducing the amount of the resinous part on the expense of the loaded inorganic fillers. The conventional fillers comprise amorphous silica, quartz, borosilicate, alumina and zirconia[19].

Matrix Phase:

The monomer constitutes the main component of the matrix phase. Dimethacrylate-based resins are considered as the keystone of dental composites. Polymerization of methacrylate-based monomers occurred through a mechanism of a chain-growth, where high molecular weight polymers are formed rapidly in the process, which cause early vitrification[20].

Most dental resin composites have been based on viscous liquid aromatic oligomer bisphenol A-glycidyl methacrylate (Bis-GMA) which is produced from the reaction of one molecular bisphenol-A and two molecular glycidyl methacrylate. This oligomer contains reactive carbon double bonds (C=C) at each end, that can take part in free-radical polymerization reactions. Thus, produce a highly cross-linked polymer showing low water sorption and high mechanical properties. The apparent high viscosity of Bis-GMA require their dilution with a more fluid resin such as methyl methacrylate (MMA), ethylene glycol

dimethacrylate (EGDMA), triethylene glycol dimethacrylate (TEGDMA) and 1,6-hexanediol dimethacrylate (HDDMA) to achieve a degree of viscosity appropriate for fillers incorporation [15,20].

Urethane dimethacrylate (UDMA) is the most used difunctional monomers. This monomer has been used alone or in combination with other monomers such as Bis-GMA and TEGDMA. The advantages of UDMA have been reported to be lower viscosity and a greater flexibility of the urethane linkage, which may improve the fracture toughness of resin composites[20]. The chemical structure of the most common base and diluent monomers are shown in Figure 3.

Nowadays, most of the commercially available dental composites were utilized monomer systems in which all or part of Bis-GMA is replaced by the lower viscosity aliphatic or aromatic dimethacrylates. On the other hand, some companies use other varieties of monomers (as silorane-based matrix) to improve the properties of their resin composite materials. Methacrylate monomers react via an addition polymerization reaction to form a highly cross-linked structure when light of appropriate wavelength and intensity is applied[20,21]. Therefore, the resin matrix has an important influence on the chemical and physical properties of resin. Figure 4 represent a digramatic illustration of polymerization shrinkage among traditional dimethacrylate-based resin, Bis-GMA resin and silorane-based resin.
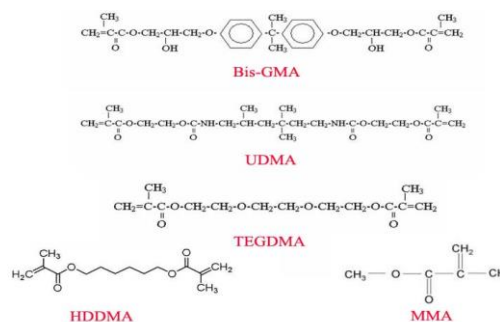

Fig. 3. Chemical structure of the basic monomers of dimethacrylate-based dental resin composites.
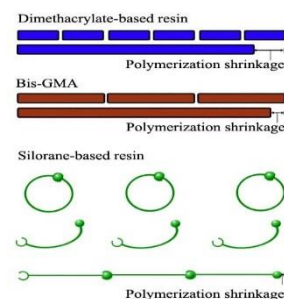

Fig. 4. Diagrmatic illustration of polymerization shrinkage of conventional dimethacrylate-based resin, Bis-GMA resin, and silorane-based resin.

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Coupling Agent:

Incorporation of filler particles into the resin matrix significantly improves the properties of the matrix material if the filler particles are well bonded to the matrix. A coupling agent is required to enable bonding of filler particles to the matrix. Organosilanes such as gamma-methacryloxy propyl trimethoxy silane (γ-MAPS) are the most used coupling agents[19].

Photo-initiator

Currently the most extensively used photoinitiator in dental resin composites is camphorquinone (CQ), particularly due to its suitable reactivity and capability to initiate the process of polymerization incombination with system amine co-initiator.

Modifications of resin matrix:

The amount and types of monomer are greatly affect the polymerization shrinkage of dental composites[22]. Evolving improvements in resinous phase of the dental composites were progressed to decrease the polymerization shrinkage to the least value.

Use of thiol-ene-based monomers:

Thiol–ene monomers were developed as an alternative to methacrylate-based systems. The mechanism of polymerization relies on radical-mediated step-growth between thiol and vinyl monomer. During the initiation stage, a thiyl radical is produced, which adds to a vinyl group, leading to a carbon-centered radical. Thus, formation of a thioether and a thiyl radical. The step-growth polymerization mechanism resulting in delayed gelation compared to the chain-growth mechanism of methacrylates with a significant polymerization shrinkage reduction[23,24].

Use of silorane-based monomers:

Silorane-based resin revealed a lower polymerization shrinkage compared to the dimethacrylates such as (Bis-GMA, UDMA, and TEGDMA). Silorane molecules polymerize through cationic ring-opening intermediates, instead of free radical cross-linked polymerization of dimethacrylate monomers, which in turn may produce polymerization shrinkage values less than 1%[25]. The epoxy ring of the oxirane monomer rings are responsible for the reduced polymerization shrinkage. During polymerization it is opened to produce a linear chain with volumetric expansion that may compensate for volumetric shrinkage to some extent[26,27].

Modification of inorganic fillers:

Generally, the increase in the inorganic filler load on the expense of the resin matrix will consequently reduce the polymerization shrinkage. However, the addition of inorganic fillers to polymer resin has a certain limitation in order to achieve an adequate wettability of the resinous matrix to the fillers without creation of weak interface between these two phases[19].

Inorganic fillers modification is considered as the ultimate goals in evolution of dental resin composites, because filler type, load, size, and distribution will greatly affect the dental composites clinical success. Vast approaches have been done to improve the filler component load and quality[21].

Incorporation of nanogels:

Nanogels are a prepolymerized polymer in nanosized that cross-linked with the resin matrix and chemically attached to the inorganic filler surface, forming interphase structure between resin matrix and fillers. Nanogel prepolymer utilization in resin composite manufacturing considered as a versatile approach promote the incorporation of inorganic filler into resin matrix. Although, their polymeric origin, nanogels have been exposed to enhance mechanical properties of nanogel-modified composites. Moreover, they reduce the polymerization shrinkage associated with high nanogel content[28].

Incorporation of bioactive nano-sized fillers:

Polymerization shrinkage of dental resin composite could be reduced by decreasing the resin/filler ratio, which may be achieved by incorporation of more reinforcing inorganic filler, while at the same time get the unique benefit of the added fillers[29]. A novel type fillers were advocated as a possible solution to induce bioactivity, remineralization capability and to enhance mechanical feature of the restoration such as: Nano-hydroxyapatite[30–33], bioactive glass[34,35], calcium silicates[36], calcium phosphates[37], and other calcium-based derivative[38–40].

2. Conclusions

Polymerization shrinkage of dental resin composites might be affected by the matrix content, nature of polymerization reaction, inorganic fillers content and ratio. Polymerization shrinkage with subsequent gap formation at tooth/restoration interface remains the biggest challenge on placing resin-based composite restorations. Evolving improvements associated with dental polymeric materials and adhesives improved the longevity of resin-based dental composites via reduction of polymerization shrinkage and enhancement of mechanical properties. The incorporation of reinforcing inorganic fillers on the expense of resin matrix reduce the polymerization shrinkage. Modification of the resin phase have a

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greater influence to decrease the polymerization shrinkage, than modification in the filler phase as the resin phase is responsible directly in the shrinkage of resin based composite restorations due to polymerization reaction.

3. Conflicts of interest

There are no conflicts to declare.

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