Low-Shrink Monomers for Dental Restorations

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Abstract: The main disadvantages of resin-based composites (RBCs) for use in load-bearing posterior restorations include the polymerization shrinkage following curing and inadequate wear resistance in service. These properties are largely influenced by the monomer system and research is currently being undertaken to decrease polymerization shrinkage and improve resin wear characteristics in an attempt to increase RBC restoration longevity. The scope of the current review will identify the development of resin-based restoratives, indicating the reported advantages and disadvantages of resin types routinely used in dental practice today and review the most recent advancements in resin technology.

Clinical Relevance: Composites with low-shrink monomers could provide better ease of use for clinicians.

HISTORICAL PERSPECTIVES

Resin-based restoratives have been used extensively in dentistry for the past seven decades since the introduction of commercially available methyl methacrylate resins in the late 1930s. The subsequent advancements in resin chemistry remain the basis for the most popular dental resins commonly used in dental practices today. Alterations in composition and manipulation of dental resins have influenced a wide range of applications in modern restorative dentistry so that resins can be used for the following:

- in the construction of complete and partial dentures;
- in the construction of crowns;
- in the construction of bridges;
- as sealants; and
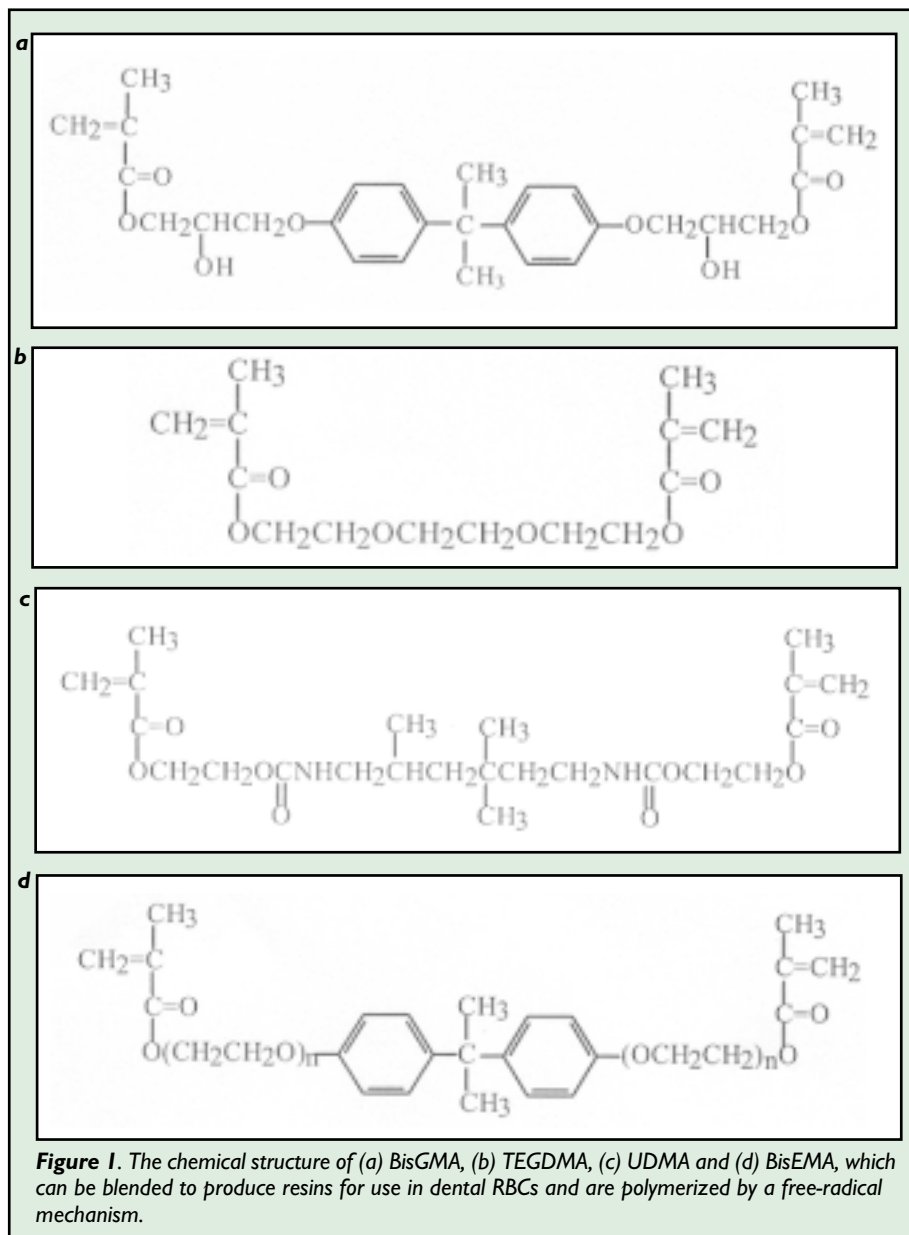- as direct composite filling materials.

Commercially available resin-based composites for use as direct filling materials were introduced in the 1960s following the pioneering work of R.L. Bowen, the Associate Director of the American Dental Association Research Unit at the National Bureau of Standards. Bowen[1] patented a novel RBC composed of 25 wt% (weight percent) polymerizable resin and 75 wt% quartz or alumino-silicate glass filler which was to revolutionize existing resin-based dental technology. The pale yellow, highly viscous dimethylmethacrylate monomer was synthesized from the reaction of bisphenol-A and glycidyl methacrylate and given the acronym BisGMA (Figure 1a). BisGMA is a highly rigid and viscous material that was identified to be unsuitable for the incorporation of filler particles and manipulation of the material in cavity placement. Further investigations[2] reported the necessity for the addition of a co-monomer, triethyleneglycol dimethacrylate (TEGDMA) (Figure 1b) to decrease the viscosity of the mixture and aid incorporation of the filler particles. It was these methacrylate monomers that provided the potential for increased mechanical and physical properties compared with alternative, non-metallic materials of that period. In fact, methacrylate-based composites and their derivatives remain the most commonly used RBCs in dentistry today with commercially successful composites, such as Z100 (3M ESPE Dental Products, St Paul, MN, US) utilizing these resin combinations. The patient demand for increased aesthetics and the potential of RBCs as an amalgam replacement have driven increased research into many aspects of resin technology. If RBC restoratives are to provide clinical longevity similar to amalgam fillings, then such materials must provide mechanical properties that withstand occlusal forces and physical properties that do not compromise the adhesive bond at the interface of tooth and restoration.

METHACRYLATE-BASED MONOMERS

The organic matrix of many commercially available light-cured RBCs used in clinical practice are based on methacrylate chemistry. Advancements in filler particle

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Figure 1. The chemical structure of (a) BisGMA, (b) TEGDMA, (c) UDMA and (d) BisEMA, which can be blended to produce resins for use in dental RBCs and are polymerized by a free-radical mechanism.

and resin technology have provided RBCs with sufficient mechanical properties that may suggest such materials as a replacement for amalgam. However, physical properties of methacrylate-based RBCs, namely polymerization shrinkage, remain inadequate if RBC restorations are to exhibit clinical longevity similar to amalgam. Placement of light-activated, resin-based restoratives involves light irradiation to initiate polymerization of the constituent monomers. The associated polymerization shrinkage of such commercially available methacrylate-based RBCs has been

reported to be in the region of 2–4%.[3-5] Following irradiation, the free-radical polymerization of dimethacrylate monomers is accompanied by the closer packing of molecules leading to bulk contraction, where the gelation point of an RBC occurs when the viscous flow of the curing monomer is unable to keep up with the curing contraction.[6] Consequently, this post-gel contraction of the RBC is constricted by the strength of the adhesive bond at the tooth-restoration interface and, as a result, polymerization shrinkage of the composite material may be manifested as shrinkage stress. The resultant stress may:
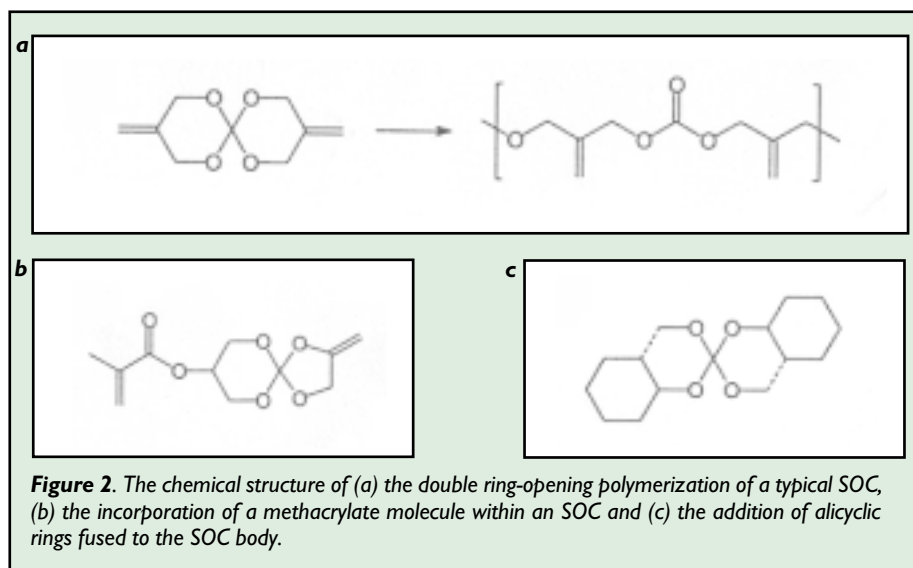
- compromise the synergism between the tooth and restoration interface;[7]
- increase the likelihood of mechanical failure;[8]
- permit the ingress of bacteria, which may result in pulpal irritation;[9] or
- result in cuspal deflection.[10]

Polymerization shrinkage of resins are controlled by the viscosity of the material, whereby a lower resin viscosity (also required for the incorporation of filler particles) would contain a higher number of carbon-carbon double bonds and therefore an increased conversion to the polymer state, resulting in an increased volumetric shrinkage.

Previous reports have suggested that the incorporation of a less viscous resin than BisGMA, urethane dimethacrylate (UDMA) (Figure 1c) may provide RBCs with improved mechanical properties[11,12] and derivatives of BisGMA were also developed, such as bisphenol-A ethoxylated dimethacrylate (BisEMA) (Figure 1d). Commercial products, namely Filtek™ Z250 (3M ESPE Dental Products, St Paul, MN, US), have used such developments in resin technology in an attempt primarily to decrease polymerization shrinkage and increase strength compared with its predecessor, Z100. Although desirable mechanical properties were maintained, it was suggested that decreased water sorption was the only improvement to conventional BisGMA resins.[13]

BICYCLIC MONOMERS

In an attempt to eliminate polymerization of polymeric materials, scientists have investigated the use of monomers that do not decrease in volume on polymerization. Bailey[14] reported the homo-polymerization of bicyclic ring-opening monomers including spiro-orthocarbonate (SOC) monomer resins (Figure 2a), which resulted in no shrinkage or even expansion on polymerization. The volumetric expansion was suggested to be a result of a double spiro-cyclic ring opening of the SOC molecule which has been previously instrumental in the development of high strength industrial adhesives and manufacture of precision

Figure 2. *The chemical structure of (a) the double ring-opening polymerization of a typical SOC, (b) the incorporation of a methacrylate molecule within an SOC and (c) the addition of alicyclic rings fused to the SOC body.*

castings.[15] Thompson *et al.*[16] first investigated the incorporation of SOCs into dental composites and attempted to combine the strength of conventional resins with the decreased shrinkage (or even expansion) of SOC monomers. However, the SOC formulation did not allow for the incorporation with BisGMA resins and polymerization of the resin mixture resulted in decreased monomer conversion, hence reduced molecular cross-linking of the polymer and decreased mechanical properties. Stansbury[17] reported SOCs with decreased melting points and variations in ring size which permitted the incorporation into methacrylate resins, namely BisGMA and TEGDMA, that were able to co-polymerize by a cationic and a free-radical mechanism (Figure 2b). This formulation exhibited a polymerization shrinkage of 2.4% compared with 3.9% for the methacrylate-based co-monomer control. Although a reduction in shrinkage was identified, such high values could produce the inherent disadvantages associated with the contraction stress of methacrylate resins commonly used in clinical practice today.

Further structural improvements to SOC resins were investigated by Byerley *et al.*[18] The SOC formulations exhibited in Figure 2c contained additional alicyclic rings (containing no carbon to carbon double bonds) fused to the SOC body. Polymerization of the monomer proceeded by a cationic mechanism where a double-

ring opening mechanism involved the breaking of two covalent bonds to form one new bond.[14,15] SOC formulations polymerized by an initial cationic mechanism compared with the non-opening free radical polymerization associated with methacrylate monomers. This eliminated polymerization shrinkage and produced an expansion of 3.5%.[18] However, SOCs exhibit significantly less reactivity than methacrylate mixtures which may have resulted in inadequate saturation of SOC rings, decreased cross-linking and therefore decreased

mechanical properties.[19] Consequently, composites manufactured from SOC technology are not routinely marketed because of these difficulties.
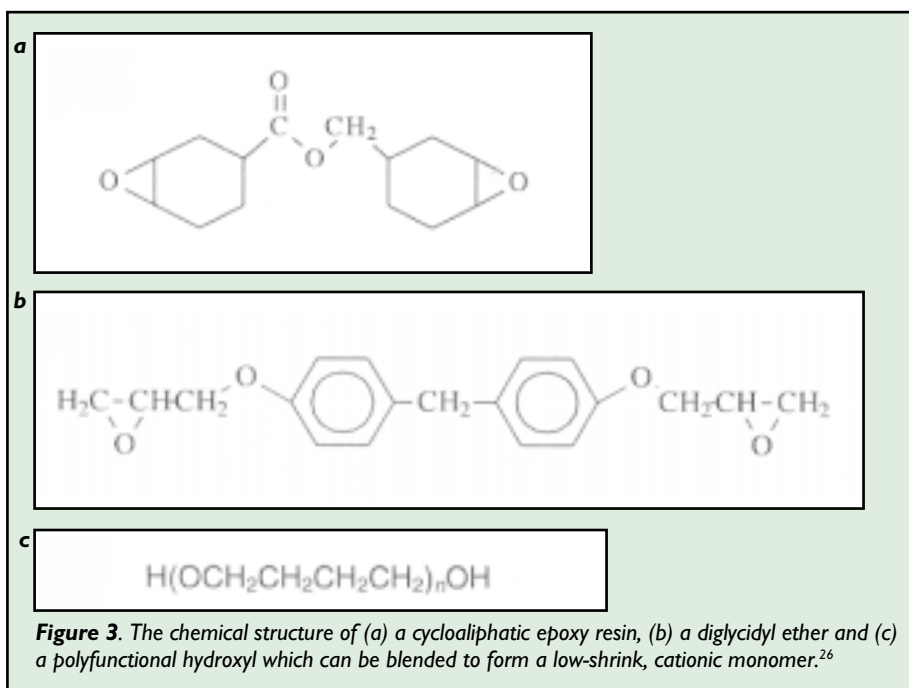
EPOXY-BASED MONOMERS

As well as his pioneering work, which introduced BisGMA/TEGDMA-based resins to dentistry,[2] Bowen[20] also realized that newly developed synthetic resins of that period, such as epoxy-based monomers, would find considerable application to dental materials. Bowen[20] reported the following promising results of an epoxy resin filled with fused silica:

● a thermal expansion equal to that of dentition;
● good adhesive properties; and
● colour stability.

However, slow reaction rates of the epoxy monomer were found to be unsuitable for use as a direct filling material. Consequently, attention turned to the development of methacrylate-based RBCs (BisGMA/TEGDMA) and improvements to epoxy-based dental composites would not be realized until several decades later.

Recently, the investigation of novel monomer systems has once again identified the potential of epoxy-based

Figure 3. *The chemical structure of (a) a cycloaliphatic epoxy resin, (b) a diglycidyl ether and (c) a polyfunctional hydroxyl which can be blended to form a low-shrink, cationic monomer.*[26]

monomers and their application to dental RBCs. Epoxy resins are reported to have significantly decreased shrinkage on polymerization compared with methacrylate monomers (0.3 vol% for an unfilled cycloaliphatic epoxy resin[19] and 7.9 vol% for an unfilled BisGMA/TEGDMA resin,[21] respectively). Following the unsuccessful attempts of combining methacrylates with SOC monomers to decrease polymerization shrinkage of experimental dental composites,[16,17] properties of co-monomer mixtures of SOCs and epoxy resins have been considered.[22–24] Although polymerization shrinkage was decreased (due to the combination of slight shrinkage of the epoxy and expansion of the ring-membered SOCs) and water sorption reduced, the addition of SOC to the epoxy resin further increased the cure-time of the monomer.[24]

The applications of cycloaliphatic epoxy resins have been a subject of interest since the unsuccessful research of SOC-containing materials. Epoxy resins have been formulated with polyfunctional hydroxyls (polyols) (Figure 3) to produce a reactive species that will cure by a cationic mechanism using conventional dental curing-lights to produce a low-shrink composite.[25] Previous investigations have suggested decreased polymerization shrinkage[26] and an associated reduction in shrinkage stress compared with methacrylate-based RBCs.[27] Such epoxy/polyol resin formulations are known to exhibit 'living' polymerization, where the reactive species do not become extinguished as quickly as the free radicals contained within methacrylate resins.[23] Current research has suggested a decrease in degree of conversion (DC) of an experimental epoxy-based RBC (Figure 3) compared with the DC of a commercially available methacrylate-based RBC after periods of 0.1, 0.5 and 1 h following initial irradiation.[28] The reduced conversion rates within the first hour of service may suggest some relief of contraction stress at adhesive junctions between tooth and restoration. After 24 hours, the significant increase in DC and flexural strength of the novel RBC may also suggest an increase in cross-linking of the polymer, hence promising mechanical properties for use in the oral cavity. However, decreased conversion rates within the first hour following irradiation may compromise the flexural strength of material that might prove inadequate under masticatory loading.

SUMMARY

In general, the development of resins for use in RBC restorative materials has been slow. Dentists commonly use similar base-resins, such as BisGMA, which have been utilized for 40 years, and it is only since the last decade that novel monomer systems for RBCs have appeared in the literature. Whilst research continues in an attempt to develop novel, low-shrink RBCs, there is currently no commercially available solution to polymerization shrinkage. In an attempt to improve the properties of existing RBCs, manufacturers will continue to manipulate derivatives of existing resins and alter filler loading and morphology. Researchers may also endeavour to use different light-curing methods, such as soft-start polymerization, or suggest more effective placement techniques, such as the use of flowable composites or lining materials, to alleviate the associated contraction stress on placement. Substantial amounts of time, money and research are required to develop innovative materials and for these reasons it is suggested that it may be several years before innovative, low-shrink resin mixtures for RBCs are available for use in general dental practice.

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